Electrogenerated base promoted synthesis of *N*-substituted-4-hydroxy-4-methylthiazolidine-2-thione derivatives

Khalil Tissaoui, Noureddine Raouafi* and Khaled Boujlel

Laboratoire de Chimie Analytique et Electrochimie, Faculté des Sciences de Tunis, Université Tunis El-Manar, Campus Universitaire 2092 Tunis, Tunisia

Electrochemically-generated basic species from the reduction of acetonitrile assisted the condensation of carbon disulfide, primary arylmethylamines and chloroacetone to yield the corresponding *N*-substituted-4-hydroxy-4-methylthiazolidine-2-thione derivatives. In some cases, dehydration reaction led to the *N*-substituted-4-methylthiazole-2(3*H*)-thione analogues. The effect of the electrogenerated base amount on the reaction yield was also studied.

Keywords: electrogenerated bases/anions, carbamodithioates, electrosynthesis, cyclisation, thiazolidine-2-thione, thiazole-2-thione

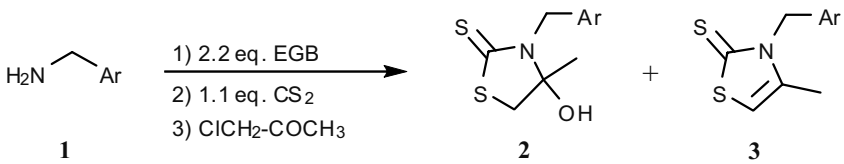
Numerous new regulations and policies such the EPA standards for polluting contaminants and European program REACH for hazardous chemical registration are aimed to limit and eventually to banish the use of polluting and hazardous solvents and corrosive reagents from chemical processes.[1-4] Alternative methods for organic compounds preparation are therefore widely solicited. Recently, an efficient and convenient one-pot electrosynthesis of tetrahydro-1-benzo[*b*] pyran derivatives starting from malononitrile, aryl aldehydes and dimedone without involvement of an added base was reported.[5] Feroci *et al.* reported numerous preparations and synthetic applications of carbamates and oxazolinones under mild conditions by cyanomethyl *in situ* electrogenerated base (EGB).[6,7] One of the most striking advantages of electrochemical methods is the excellent control of the base strength depending on the choice of the solvent acidity. Furthermore, the amount of the electrogenerated base is a function of the applied current densities and the duration of the electrolysis which also could be also tuned.[8]

It is well established that the electrochemical reduction of dry acetonitrile with, or without, the addition of a probase such as azobenzene or cyanomethyl anion precursors like cyanomethyl triphenylphosphonium[9] in the presence of quaternary ammonium salt as a supporting electrolyte produces the corresponding cyanomethyl anion, a strong base entity, with a p*K*a value of 31.3,[10] which is strong enough to remove weak acidic protons and is also able to act as a nucleophile.[11,12] The anion could be easily stabilised as Grignard-type species by association with the anodically-generated cation from the oxidation of a sacrificial metal anode.[13]

In the last few years, we have devoted much effort to develop an alternative synthesis of carbamodithioate derivatives from primary and secondary amines and carbon disulfide using an *in situ* electrogenerated base.[14] We report here the synthesis of *N*-substitued-4-hydroxy-4-methylthiazolidine-2-thione derivatives starting from various arylmethylamines, carbon disulfide and chloroacetone promoted by electrochemically generated bases. These products possess a large spectrum of applications such as a subunit for material design through charge transfer complexes formation,[15] as a class of versatile chiral auxiliaries for asymmetric synthesis,[16] and as intermediates for organic synthesis.[17,18]

Using an undivided electrochemical cell, fitted with a magnesium rod as a sacrificial anode and a stainless steel grid cathode and maintained under inert atmosphere of argon, the electrolysis of anhydrous acetonitrile, under galvanostatic conditions, yielded cyanomethyl anions/bases. The electrolysis of acetonitrile was stopped when the desired amount of base was formed. The amount was calculated with respect to the quantity of amine to be introduced. Once the electrolysis finished, the amine was introduced in the basic medium followed by the addition of carbon disulfide provoking a dramatic change in colour of the solution from yellowish to dark-red. Finally, chloroacetone was added, the solution was allowed to reach room temperature and kept under continuous stirring overnight. Final work-up and column chromatography over silica gel afforded the products **2** and **3** (Table 1) in good yields (Scheme 1).

A stabilised carbamodithioate intermediate was formed during the reaction of carbon disulfide and the amine promoted by the electrogenerated cyanomethyl and amino-crotonitrile anions/bases.[13,14] The carbamodithioate anion was probably stabilised by ion-pairing with the electrogenerated magnesium cations from the sacrificial magnesium anode. Alkylation of the intermediate with chloroacetone gave the acyclic intermediate which immediately underwent ring closure to give product **2**. Attempts failed to isolate the acyclic intermediate even if 0.5 equivalents EGB were used with respect to the amine. For all the studied amines, the highest reaction yields were obtained for an amount of electrogenerated base equal to 2.2 equivalents. In some cases, the product **2** underwent dehydration reaction favoured by the excess of formed EGB to give the product **3**. The formation of compound **3** from **2** has been confirmed by treating substrate **2** by EGB which gave product **3** in high yields. A series of products **2** and **3** was synthesised by applying the latter conditions *i.e.* consumption of 2.2 Faradays, to form the same amount of EGB, followed by a subsequent addition of amine, carbon disulfide and chloroacetone (Table 1).



1 2 3

Scheme 1

* Correspondent. Noureddine.raouafi@gmail.com//rdnnin@fst.rnu.tn

Table 1 Synthesised *N*-substituted-4-hydroxy-4-methylthiazolidine-2-thione **2** and *N*-substituted-4-methylthiazole-2-thione **3**

Entry	Starting amine R–CH_2–NH_2; R =	**Q**[a]	**2**[b]/%	**3**[b]/%
a	Phenyl	2.2	85	11
b	Pyridin-2-yl	2.2	68	–[c]
c	2-Chlorophenyl	2.2	53	9
d	4-Methylphenyl	2.2	46	32
e	4-Fluorophenyl	2.2	79	–[c]
f	4-Methoxyphenyl	2.2	54	–[c]
g	4-Chlorophenyl	2.2	65	–[c]
h	3-Piperonyl	2.2	72	–[c]

[a]The consumed quantity of electricity represents the number of Faradays per mole of amine (F mol^{-1}).
[b]The yield was calculated in regard to the starting amine.
[c]Product not isolated.

Comparatively to our previous preparation method for the carbamodithioate[14] using a two-compartment electrochemical cell, inox steel grid as cathode and carbon graphite as anode, improvement of the reaction yield was noticed that could be mainly attributed to two factors: (i) the replacement of a divided electrochemical cell by an undivided one allowed the application of a higher current densities since the ohmic drop was less important; and (ii) unlike the magnesium anode, the oxidation of graphite carbon did not produce any stabilising cations for the electrogenerated anonic species. Note that when a small quantity of the same amine was used, the electrolysis time of acetonitrile was shortened and less basic species were re-protonated affording higher yields of compound **2a** (see Tables 1 and 2).

The number of Faradays with respect to the quantity of amine, *i.e.* consumed amount of electrons during the electrolysis of acetonitrile being proportional to the number of mole of the electrogenerated base, affected the yield of the reaction. This influence was studied in a typical procedure using benzylamine as model compound. The standardised procedure consisted of the electrolysis of the acetonitrile by passing through the desired number of Faradays, and then benzylamine was introduced, followed half an hour later by carbon disulfide and finally chloroacetone. The solution was stirred overnight and followed by a standard workup to yield product **2a** (Table 2).

The yield of the reaction increased with the amount of the used electrogenerated base *i.e.* the number of Faradays. For an amount of the base equal to 2.0–2.5 equivalents with respect to benzylamine, the yield reached 85–87% which was a good compromise between the reaction time and the consumed energy and the Faradic yield *i.e.* chemical yield divided by number of used Faradays was *ca* 40%. Furthermore, when a five-fold excess of base was used per mole of amine, the yield was only improved *ca* 7% and the Faradic yield decreased to *ca* 19%.

As compared to classical synthetic methods, the present one using electrogenerated bases shows several advantages such as: (i) no additional base was required because of the *in situ* base generation; (ii) milder reaction conditions and use of cheap and readily available reagents; (iii) fair to very good yields; (iv) no hazardous chemicals and polluting by-products resulting from the addition of base or probase; (v) no sophisticated electrochemical instrumentation and cell needed; and (vi) an easy work-up procedure.

Table 2 Variation of the yield of **2a** as a function of the consumed number of Faradays in respect to the quantity of amine

Entry	**Q**/F mol^{-1}	Yield of **2a**/%
1	0.5	61
2	1.0	71
3	1.5	82
4	2.0	85
5	2.5	87
6	3.0	89
7	4.0	92
8	5.0	93

Experimental

Melting points were determined with an Electrothermal 9100 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Advance 250 or 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. IR spectra were measured using Bruker Alpha ATR spectrometer; samples were dissolved in $CHCl_3$. High resolution mass spectra were performed by the ICSN, Gif-sur-Yvette, Paris, France. Only products **2a** and **3a** have been previously described[19] and others similar compounds have also been reported.[20,21] Anhydrous acetonitrile (10 ppm, anhydroscan®) was purchased from Labscan and dried over activated alumina. All chemicals were purchased from Sigma-Aldrich and are used without further purification.

Electroorganic synthesis of N-substituted-4-hydroxy-4-methyl thiazolidine-2-thione **2**

In a typical reaction, 90 mL dry acetonitrile solution of tetrabutylammonium tetrafluoroborate (0.01 M) as supporting electrolyte in an undivided cell fitted with a sacrificial magnesium rod as an anode and a stainless steel grid (20 cm^2) as cathode was subjected to electrolysis at a constant current density (I = 80 mA cm^{-2}, 7.0 h, 2.2 F $mole^{-1}$ with respect to the quantity of amine to be added). The cell was cooled to –20 °C by immersing it in Lauder refrigerating system. During the electrolysis, the system was maintained under inert atmosphere by continuous bubbling of argon. The electrolysis was stopped after the formation of 2.2 equivalents of cyanomethyl anion with respect to the amine; 10.0 mmol of the amine was introduced first and, one hour later, 2.2 equivalents of carbon disulfide were added, and the solution turned immediately from pale yellow to dark red. For the second set of experiments summarised in Table 2, 5.0 mmol of benzylamine, 11.0 mmol of CS_2 and 11.0 mmol of chloroacetone were used, respectively. After one hour of stirring, 2.2 equivalents of chloroacetone were added. The cooling bath was removed and the solution was allowed to reach room temperature and kept under continuous stirring overnight to ensure the tandem alkyation–cyclisation reaction where it is possible. The excess of acetonitrile was removed in rotatory evaporator and the residue was diluted in 50 mL of water and extracted three times with 20 mL of diethyl ether. The organic layer was washed with 20 mL of water and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel 60. A mixture of ethyl acetate/hexanes (3:7) was used as eluant. The resulting yellowish solid was filtered and recrystallised from chloroform. All the products are known and were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, IR spectroscopy, melting point, in some cases, HRMS and elemental analysis.

3-benzyl-4-hydroxy-4-methylthiazolidine-2-thione (**2a**): M.p. 106–107 °C (lit. 102–103); yield: 85%. IR (cm^{-1}, $CHCl_3$) ν: 3570 (OH); 3120–2985 (CH); 1605 (C=C); 1210 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (d, 3H, CH_3, *J* = 10.7); 2.14 (br, 1H, OH); 3.47 (dd, 2H, CH_2, *J* = 12.0 Hz); 5.11 (dd, 2H, CH_2, *J* = 15.4 Hz); 7.24–7.40 (m, 5H, $H_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.8; 42.1; 48.8; 97.6; 126.6; 127.3; 127.5; 128.7; 128.9; 136.9; 197.2 (C=S). GC-MS: *m/z* = 239 (M^+); 221 (M^+-H_2O); 188 (M^+-H_2O-HS); 91 ($C_7H_7^+$); 77 ($C_6H_5^+$). HRMS Calcd for $C_{11}H_{13}NOS_2$: 239.0439. Found 239.0475.

4-hydroxy-4-methyl-3-[(pyridin-2-yl)methyl]thiazolidine-2-thione (**2b**): M.p. 112–113 °C; yield: 68%. IR (cm^{-1}, $CHCl_3$) ν: 3575 (OH);

3125–2980 (CH); 1610 (C=C); 1214 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.74 (s, 3H, CH_3); 2.30 (br, 1H, OH); 3.41 (dd, 2H, CH_2, J = 12.1 Hz); 5.12 (dd, 2H, CH_2, J = 15.7 Hz); 7.26 (t, 1H, $CH_{arom.}$); 7.52 (d, 1H, $CH_{arom.}$); 7.73 (t, 1H, $CH_{arom.}$); 8.44 (d, 1H, $CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.8; 43.1; 49.4; 96.8; 122.9; 124.5; 138.1; 148.2; 154.5; 196.2 (C=S). GC-MS: m/z = 240 (M^+); 222 (M^+-H_2O); 189 (M^+-H_2O-HS); 92 ($C_6H_6N^+$). HRMS Calcd for $C_{10}H_{12}N_2OS_2$: 240.0391. Found 240.0404.

3-(2-chlorobenzyl)-4-hydroxy-4-methylthiazolidine-2-thione (**2c**): M.p. 115–116 °C; yield: 53%. IR (cm^{-1}, $CHCl_3$) ν: 3565 (OH); 3110–2985 (CH); 1604 (C=C); 1206 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.45 (s, 3H, CH_3); 3.11 (br, 1H, OH); 3.36 (dd, 2H, CH_2, J = 12.0 Hz); 4.97 (dd, 2H, CH_2, J = 15.4 Hz); 6.71–7.25 (4H, $CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.8; 41.2; 59.2; 97.0; 128.8; 129.5; 133.3; 135.8; 160.2; 197.2 (C=S). HRMS Calcd for $C_{11}H_{12}ClNOS_2$: 273.0049. Found 273.0083.

4-hydroxy-4-methyl-3-(4-methylbenzyl)-thiazolidine-2-thione (**2d**): M.p. 138–139 °C; yield: 46%. IR (cm^{-1}, $CHCl_3$) ν: 3574 (OH); 3124–2982 (CH); 1601 (C=C); 1213 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.53 (s, 3H, CH_3); 2.32 (s, 3H, CH_3); 3.31 (dd, 2H, CH_2, $^2J_{H\text{-}H}$=11.7 Hz); 4.94 (dd, 2H, CH_2, dd, J = 16.6 Hz); 7.17 (dd, 4H, J = 3.0 Hz; $CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.6; 21.1; 29.7; 49.9; 106.1; 126.6; 129.5; 131.8; 137.6; 140.1; 189.2 (C=S). HRMS Calcd for $C_{12}H_{15}NOS_2$: 253.0595. Found 240.0613.

3-(4-fluorobenzyl)-4-hydroxy-4-methylthiazolidine-2-thione (**2e**): M.p. 122–123 °C; yield: 79%. ^{1}H IR (cm^{-1}, $CHCl_3$) ν: 3557 (OH); 3111–2981 (CH); 1603 (C=C); 1217 (C=S). NMR (300 MHz, $CDCl_3$) δ: 1.50 (s, 3H, CH_3); 3.34 (dd, 2H, CH_2, J = 12.4 Hz); 4.98 (dd, 2H, CH_2, dd, J = 16.0 Hz); 6.96 (mu, 2H, $CH_{arom.}$); 7.32 (mu, 2H, $CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.8; 42.1; 47.4; 97.6; 115.7; 128.6; 138.1; 160.5; 197.2 (C=S). HRMS Calcd for $C_{11}H_{12}FNOS_2$: 257.0344. Found 257.0356.

4-hydroxy-3-(4-methoxybenzyl)-4-methylthiazolidine-2-thione (**2f**): M.p. 154–155 °C; yield: 54%. IR (cm^{-1}, $CHCl_3$) ν: 3576 (OH); 3110–2984 (CH); 1607 (C=C); 1223 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.47 (s, 3H, CH_3); 3.33 (dd, 2H, CH_2, J = 11.4 Hz); 3.81 (s, 3H, CH_3); 5.02 (dd, 2H, CH_2, J = 15.5 Hz); 6.72 (d, 2H, J = 8.5 Hz, $CH_{arom.}$); 7.26 (d, 2H, J = 8.5 Hz, $CH_{arom.}$). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ: 26.1; 42.1; 47.7; 49.8; 55.4; 97.8; 106.5; 114.1; 114.3; 128.3; 129.0; 140; 159.1; 196.9. HRMS Calcd for $C_{12}H_{15}NO_2S_2$: 269.0544. Found 269.0578.

3-(4-chlorobenzyl)-4-hydroxy-4-methylthiazolidine-2-thione (**2g**): M.p. 111–112 °C; yield: 65%. IR (cm^{-1}, $CHCl_3$) ν: 3572 (OH); 3112–2983 (CH); 1602 (C=C); 1214 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.51 (s, 3H, CH_3); 3.42 (dd, 2H, CH_2, J = 11.1 Hz); 5.01 (dd, 2H, CH_2, J = 16.6 Hz); 7.22 (2H, J = 8.1 Hz, $CH_{arom.}$); 7.40 (2H, J = 8.1 Hz, $CH_{arom.}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.8; 41.7; 58.6; 98.4; 128.2; 129.1; 132.9; 135.8; 160.2; 196.6 (C=S). HRMS Calcd for $C_{11}H_{12}ClNOS_2$: 273.0049. Found 273.0085.

[(1,3-benzodioxol-5-yl)methy)]-4-hydroxy-4-methylthiazolidine-2-thione (**2h**): M.p. 144–145 °C; yield: 72%. IR (cm^{-1}, $CHCl_3$) ν: 3565 (OH); 3113–2982 (CH); 1608 (C=C); 1211(C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.50 (s, 3H, CH_3); 2.17 (br, 1H, OH); 3.35 (dd, 2H, CH_2, J = 10.8 Hz); 4.97 (dd, 2H, CH_2, J = 14.5 Hz); 5.91 (s, 2H, CH_2); 6.75–6.94 (mu, 3H, $CH_{arom.}$). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 25.7; 42.1; 47.8; 97.6; 101.1; 108.3; 120.8; 130.7; 147.0; 147.9; 197.1 (C=S). HRMS Calcd for $C_{12}H_{13}NO_3S_2$: 283.0337. Found 273.0405.

3-benzyl-4-methylthiazole-2(3H)-thione (**3a**): M.p. 88–89 °C (lit. 86–87 °C); yield: 11%. IR (cm^{-1}, $CHCl_3$) ν: 3105–2982 (CH); 1611 (C=C); 1184 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.09 (s, 3H, CH_3); 5.47 (s, 2H, CH_2); 6.22 (s, 1H, CH); 7.18–7.34 (mu, 5H, $CH_{arom.}$). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ: 15.5; 50.4; 106.1; 126.8; 127.7; 128.2; 134.8; 147.1; 189.1 (C=S).

3-(2-chlorobenzyl)-4-methylthiazole-2(3H)-thione (**3c**): M.p. 98–99 °C; yield: 9%. IR (cm^{-1}, $CHCl_3$) ν: 3100–2975 (CH); 1604 (C=C); 1175 (C=S).^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.11 (s, 3H, CH_3); 5.53 (s, 2H, CH_2); 6.26 (s, 1H, CH); 7.07–7.26 (mu, 4H, $CH_{arom.}$). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ: 15.2; 50.0; 106.1; 126.6; 127.8; 128.5; 128.8; 134.8; 140.3; 189.0 (C=S). HRMS Calcd for $C_{11}H_{10}ClNS_2$: 254.9943. Found 254.9987.

4-methyl-3-(4-methylbenzyl)thiazole-2(3H)-thione (**3d**): M.p. 121–122 °C; yield: 32%. IR (cm^{-1}, $CHCl_3$) ν: 3107–2990 (CH); 1605 (C=C); 1171 (C=S). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.08 (s, 3H, CH_3); 5.45 (s, 2H, CH_2); 6.17 (s, 1H, CH); 6.96–7.09 (mu, 4H, $CH_{arom.}$). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ: 15.6; 21.1; 59.7; 106.0; 126.7; 129.5; 131.8; 137.6; 140.1; 189.2 (C=S). HRMS Calcd for $C_{12}H_{13}NS_2$: 235.0489. Found 235.0535.

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