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This work is dedicated to the memory of Professor Yiannis Elemes

Eco-friendly synthesis of novel thiohydantoin-type sulfur-containing imidazolinone derivatives from glycine ester

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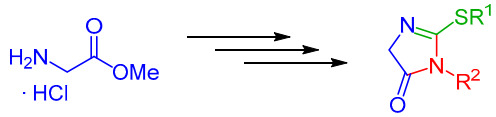

Imino derivatives of glycine ester were prepared from methyl glycinate by the known procedure and then they reacted with several amines under microwave irradiation without solvent that gave the corresponding glycine amides. By the one-component cyclocondensation, the obtained amide derivatives were transformed into thiohydantoin-type imidazolinones using solvent-free microwave procedure. All imine-ester derivatives and most of the imidazolinone derivatives were synthesized for the first time. This eco-friendly protocol can provide a suitable way for synthesizing new potentially bioactive imidazolinone derivatives.

Keywords: glycine ester, imidazolinone thiohydantoin, imidazolone, microwave irradiation, solvent-free synthesis.

One important aspect of benign chemical technologies is to remove organic solvents in chemical synthesis due to their toxicity and difficulties in containing volatile compounds. Heterocyclic synthesis methods under solvent-free conditions have developed rapidly in the past years,[1] and the number of reports on rapid, selective, and efficient transformations with a high degree of conversion of reactants to products grows every day.[2,3]

A new green method in organic synthesis is microwave (MW) radiation, which is widely used as a source of heating, as it provides spectacular accelerations, higher yields under milder reaction conditions, and higher product purities, and it reduces pollution of the environment through the use of solvent-free reaction protocols.[4–6] Solvent-free reaction conditions may provide a wide range of advantages such as improved atom utilization[7] by avoidance of common derivation procedures;[8] decreased by-product formation and, hence, decreased waste resulting from purification procedures required to separate the desired product from the impurities; and, in many instances, reduced energy utilization both in the reaction and purification stages, as well as opportunities for process intensification. Therefore, they can be used as means of waste reduction and increasing energy efficiency, which is a critical issue in the field of green chemistry and in the broader context of public health, the environment protection, and use renewable resources.[2,3]

In the past thirty years imidazolone derivatives of hydantoin (**1a**) or thiohydantoin (**1b**) (Fig. 1) have been the focus of interest for the synthetic and pharmaceutical industry due to their biological properties, including anti-convulsant,[9] antidepressant,[10] anti-inflammatory,[11] antiviral[12] (including antiHIV[13]), and antitumor[14] activities. Another important feature is that they are also effective precursors for the slow release of bioactive volatile compounds[15] and some derivatives have been used with success in crop protection. Imidazolinone herbicides, for example, imazapyr (**2**) (Fig. 1), imazapic, imazethapyr, imazamox, imazamethabenz, and imazaquin are distinguished selective herbicides that act by inhibiting the acetohydroxyacid synthase (AHAS), also known as acetolactate synthase (ALS), which is a critical enzyme for the biosynthesis of branched-chain amino acids in plants.[16] Some imidazolinones also have been found to possess fungicidal activities, for example, 5-methyl-2-(methylsulfanyl)-5-phenyl-3-(*N*-phenylamino)-3,5-dihydroimidazolin-4-one (**3**), called fenamidone, shows high fungicidal activities.[17]

The most common synthetic approach to obtain imidazolinone skeleton requires the condensation of α-amino amides with ketones or aldehydes.[18–20] Although such procedures do exist, novel methods for imidazole synthesis are still in demand. In this regard, Pospíšil and Potáček[21] reported the synthesis of a new series of substituted imidazolidin-4-ones by the reaction of equimolar amounts of *N*-substituted α-amino amides and aldehydes under solvent-free conditions, using both conventional

† Deceased.

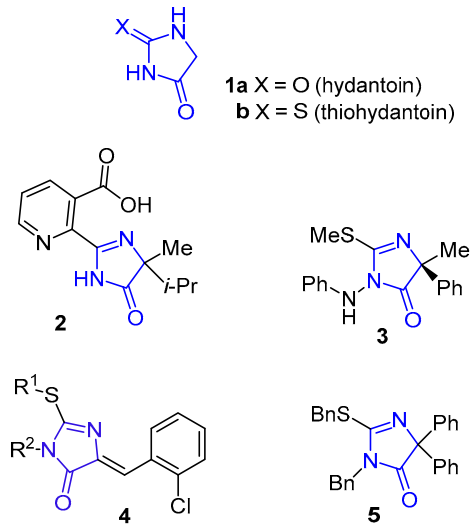

Figure 1. Structures of some hydantoin-type imidazolinones.

thermal heating and microwave irradiation. A similar method involves the conversion of an amino acid to a Schiff base of an *N*-alkylamino acid amide, followed by cyclization with benzoic anhydride to give an *N*-benzoylimidazolidin-4-one.[22]

One of the recent methods was presented by Erden et al. for a one-step synthesis of imidazolidin-4-ones based on tandem nucleophilic additions–decarboxylation–intramolecular cyclizations of Schiff base with a Leuchs' anhydride.[23] Some imidazolinone derivatives, such as 2-(alkylsulfanyl)-4*H*-imidazolin-4-ones **4**, have been synthesized by the aza-Wittig reaction of iminophosphoranes to evaluate their biological activities, and some of them exhibit herbicidal and fungicidal activities.[24]

More recently, Ramli et al. published one example of formation of heterocyclic system **5** starting from thiohydantoin derivative stirred at room temperature in DMF in the presence of catalytic amount of tetrabutylammonium bromide.[25] Talab et al. obtained 3-benzyl-2-(methylsulfanyl)imidazolin-4-one (**10a**) as an intermediate product in a few steps starting from thiocyanate and glycine amide.[26] The imidazolinone ring was used as building block to obtain 2'-^{13}C-L-histidine in high optical purity and with high ^{13}C incorporation.

In our new method, methyl *N*-[bis(alkylsulfanyl)-methylidene]glycinates **8a**–**d** were prepared from methyl glycinate (**6**) by a known procedure[27] *via* dithiocarbamates **7a**–**d**. Esters **8a**–**d** reacted with several amines under microwave irradiation without solvent that gave glycine amides **9a**–**h**. Then by the one-component cyclocondensation, amides **9a**–**h** were transformed into cyclic imidazolin-4-ones **10a**–**h** using solvent-free microwave irradiation as well (Scheme 1, Table 1).

Previously Elemes et al. have investigated the synthesis, the biological and chemical properties of pyrrolidine and pyrroline derivatives formed by 1,3-dipolar cycloaddition reactions of *N*-phenylmaleimides[28–30] and carbon fullerenes[31,32] with esterified iminoglycine derivatives **8a**–**d**. In

Scheme 1

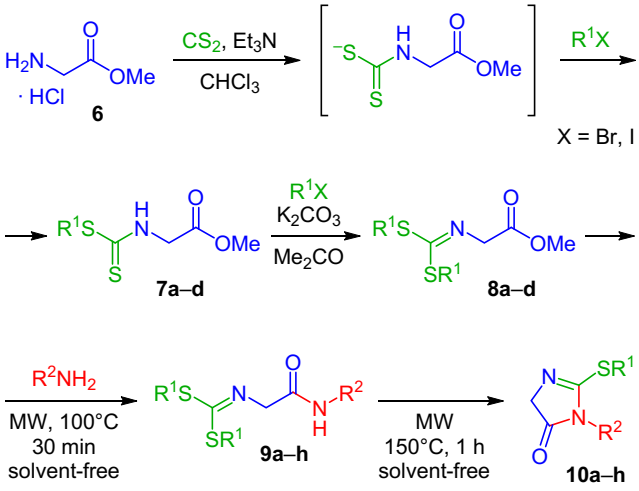

Table 1. Yields of iminoamide derivatives **9a**–**h** and sulfur-containing imidazolinone derivatives **10a**–**h**

R^1	R^2	Amide	Yield, %	Imidazolinone	Yield, %
Me	Bn	**9a**	88	**10a**	78
Et	Bn	**9b**	89	**10b**	77
Pr	Bn	**9c**	82	**10c**	74
Bu	Bn	**9d**	85	**10d**	75
Me	Bu	**9e**	91	**10e**	77
Et	Bu	**9f**	87	**10f**	74
Pr	Bu	**9g**	85	**10g**	73
Bu	Bu	**9h**	88	**10h**	70

the current study, our aim was to find a new reaction pathway for these imino ester derivatives and to explore the possibility of introducing imino ester derivatives in solvent-free microwave-assisted reaction with several amines which resulted in imino amide derivatives **9a**–**h** and lastly to elucidate the scope and limitations of this one-component cyclocondensation with formation of imidazolin-4-ones **10a**–**h** (Scheme 1, Table 1).

As shown in our previous study,[33] a reaction of imino esters **8a**–**d** with amine derivatives in THF by conventional heating resulted in the imino amide-type compounds. The best yields (64–93%) were obtained at 120°C in 4 h.[33] In continuation of our efforts to develop a more effective and rapid method for the synthesis of imino amide derivatives **9a**–**h** an alternative protocol was elaborated including microwave heating at 100°C in 30 min, thus increasing yields to 82–91%. In addition, we developed a cyclocondensation reaction to produce, for the first time, imidazolin-4-ones **10a**–**h** from imino amides **9a**–**h**, which is environmentally friendly, rapid, and highly efficient (Scheme 1, Table 1). The yields of the cyclocondensation reaction were reduced due to the presence of longer alkylsulfanyl groups on the imino amide.

The structures of new compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analyses. Spectroscopic data of the newly

synthesized compounds are in accordance with the proposed structure.

In conclusion, we developed an efficient eco-friendly method for the synthesis of imidazolin-4-one derivatives by using microwave irradiation starting from methyl glycinate. All the intermediate imino ester derivatives and almost all imidazolin-4-one derivatives were synthesized for the first time. This eco-friendly protocol can provide a suitable way for synthesizing new potentially bioactive imidazolin-4-one derivatives.

Experimental

IR spectra were recorded on a PerkinElmer Spectrum GX FTIR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-250 spectrometer (250 and 63 MHz, respectively) in $CDCl_3$, internal standard TMS. ^{13}C NMR spectra of all synthesized compounds were registered in DEPT-135 mode, ^{13}C NMR spectra of compounds **9a**–**d**, **10a**–**d** – additionally in DEPT-90 mode. Mass spectra (ESI) were recorded on a Agilent Technologies 1100 Series LC/MSD-Trap-SL spectrometer. Elemental analyses were performed on a vario MACRO cube CHNS element analyzer. All reagents and solvents were purchased from commercial suppliers and used without further purification. All microwave experiments were carried out using a monomode Anton Paar Monowave 300 microwave reactor (2.45 GHz, 850 W) in G4 microwave process vials (4 ml). Reaction temperatures were monitored by an IR sensor.

Starting compounds **8a**–**d** were prepared from methyl glycinate (**6**) by the known procedure.[27]

Synthesis of compounds 9a–h (General method). Methyl *N*-[bis(alkylsulfanyl)methylidene]glycinate **8a**–**d** (4.0 mmol) and benzyl-, *n*-butyl-, or *n*-pentylamine (4.1 mmol) were placed in a microwave process vial. The mixture was irradiated at 100°C for 30 min, then cooled by an air flow. The resulting yellow oil was chromatographed on a silica gel column using EtOAc–hexane, 1:4, as eluent. Compounds **9a**–**h** were obtained in a form of light-yellow oils. The yields are given in Table 1.

Dimethyl [2-(benzylamino)-2-oxoethyl]carbonodithioimidate (9a). IR spectrum, ν, cm^{-1}: 3379 (N–H), 3086, 3061, 3028, 3001, 2960, 2924, 2866, 1666 (C=O), 1578 (C=N), 1518, 1497, 1454, 1427, 1400, 1360, 1319, 1261, 1074, 1043, 1028, 1001, 962, 922, 800, 735, 700, 499. ^{1}H NMR spectrum, δ, ppm: 7.59 (1H, s, NH*); 7.38–7.26 (5H, m, H Ph); 4.62–4.51 (2H, m, C$\underline{H}_2$Ph); 4.02 (2H, s, CH_2CO); 2.58 (3H, s, SCH_3); 2.33 (3H, s, SCH_3). ^{13}C NMR spectrum, δ, ppm: 170.2 (C=O); 162.9 (C=N); 138.4 (C Ph); 128.7 (2CH Ph); 127.4 (3CH Ph); 55.1 (C$\underline{H}_2$CO); 43.1 (C$\underline{H}_2$Ph); 14.8 (2SCH_3). Mass-spectrum, *m*/*z*: 269 [M+H]$^+$. Found, %: C 53.64; H 5.86; N 10.76; S 23.35. $C_{12}H_{16}N_2OS_2$. Calculated, %: C 53.70; H 6.01; N 10.44; S 23.89.

Diethyl [2-(benzylamino)-2-oxoethyl]carbonodithioimidate (9b). IR spectrum, ν, cm^{-1}: 3379 (N–H), 3283, 3064, 3033, 2971, 2928, 2856, 1756, 1742, 1730, 1681, 1655 (C=O), 1578 (C=N), 1566, 1518, 1452, 1438, 1398, 1349, 1305, 1263, 1177, 1079, 1057, 1028, 960, 937, 752, 725, 698. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.53 (1H, s, NH); 7.37–7.27 (5H, m, H Ph); 4.61–4.51 (2H, m, C$\underline{H}_2$Ph); 4.02 (2H, s, CH_2CO); 3.25–3.07 (2H, m, SCH_2); 3.07–2.70 (2H, m, SCH_2); 1.37 (3H, t, *J* = 7.4, CH_3); 1.20 (3H, t, *J* = 7.2, CH_3). ^{13}C NMR spectrum, δ, ppm: 170.2 (C=O); 161.7 (C=N); 138.3 (C Ph); 128.7 (2CH Ph); 127.4 (3CH Ph); 55.3 (C$\underline{H}_2$CO); 43.1 (C$\underline{H}_2$Ph); 26.5 (SCH_2); 25.8 (SCH_2); 15.1 (CH_3); 13.7 (CH_3). Mass-spectrum, *m*/*z*: 297 [M+H]$^+$. Found, %: C 56.64; H 6.46; N 9.66; S 21.45. $C_{14}H_{20}N_2OS_2$. Calculated, %: C 56.72; H 6.80; N 9.45; S 21.63.

Di(*n*-propyl) [2-(benzylamino)-2-oxoethyl]carbonodithioimidate (9c). IR spectrum, ν, cm^{-1}: 3377 (N–H), 3033, 2962, 2923, 2870, 2843, 1752, 1730 (C=O), 1668, 1571 (C=N), 1513, 1451, 1425, 1398, 1291, 1212, 1159, 1115, 1033, 942, 876, 743, 699. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.50 (1H, s, NH); 7.37–7.27 (5H, m, H Ph); 4.57–4.51 (2H, m, C$\underline{H}_2$Ph); 4.03 (2H, s, CH_2CO); 3.06 (2H, t, *J* = 7.3, SCH_2); 2.85 (2H, t, *J* = 7.3, SCH_2); 1.81–1.67 (2H, m, $CH_2C\underline{H}_2CH_3$); 1.67–1.45 (2H, m, $CH_2C\underline{H}_2CH_3$); 1.02 (3H, t, *J* = 7.4, CH_3); 0.83 (3H, t, *J* = 7.3, CH_3). ^{13}C NMR spectrum, δ, ppm: 169.9 (C=O); 161.7 (C=N); 137.9 (C Ph); 128.4 (2CH Ph); 127.3 (3CH Ph); 55.0 (C$\underline{H}_2$CO); 42.9 (C$\underline{H}_2$Ph); 33.8 (SCH_2); 33.2 (SCH_2); 23.1 ($CH_2\underline{C}H_2CH_3$); 21.8 ($CH_2\underline{C}H_2CH_3$); 13.2 (CH_3); 13.0 (CH_3). Mass-spectrum, *m*/*z*: 325[M+H]$^+$. Found, %: C 59.04; H 7.36; N 8.96; S 19.35. $C_{16}H_{24}N_2OS_2$. Calculated, %: C 59.22; H 7.45; N 8.63; S 19.76.

Di(*n*-butyl) [2-(benzylamino)-2-oxoethyl]carbonodithioimidate (9d). IR spectrum, ν, cm^{-1}: 3382 (N–H), 3068, 3029, 2967, 2923, 2870, 2852, 1748, 1681 (C=O), 1672, 1571 (C=N), 1513, 1464, 1460, 1433, 1402, 1380, 1358, 1309, 1274, 1106, 1075, 1031, 942, 902, 862, 800, 738, 699. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.50 (1H, s, NH); 7.36–7.28 (5H, m, H Ph); 4.55–4.53 (2H, m, C$\underline{H}_2$Ph); 4.03 (2H, s, CH_2CO); 3.07 (2H, t, *J* = 7.3, SCH_2); 2.88 (2H, t, *J* = 7.4, SCH_2); 1.71–1.64 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 1.55–1.49 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 1.47–1.39 (2H, m, $(CH_2)_2C\underline{H}_2CH_3$); 1.27–1.21 (2H, m, $(CH_2)_2C\underline{H}_2CH_3$); 0.94 (3H, t, *J* = 7.3, CH_3); 0.83 (3H, t, *J* = 7.3, CH_3). ^{13}C NMR spectrum, δ, ppm: 170.2 (C=O); 162.0 (C=N); 138.2 (C Ph); 128.7 (2CH Ph); 127.4 (3CH Ph); 55.3 (C$\underline{H}_2$CO); 43.2 (C$\underline{H}_2$Ph); 31.9 (2SCH_2); 31.3 ($CH_2\underline{C}H_2CH_2CH_3$); 30.7 ($CH_2\underline{C}H_2CH_2CH_3$); 22.1 ($(CH_2)_2\underline{C}H_2CH_3$); 21.8 ($(CH_2)_2\underline{C}H_2CH_3$); 13.6 ($CH_3$); 13.5 ($CH_3$). Mass-spectrum, *m*/*z*: 353 [M+H]$^+$. Found, %: C 61.64; H 8.26; N 7.96; S 18.25. $C_{18}H_{28}N_2OS_2$. Calculated, %: C 61.32; H 8.01; N 7.95; S 18.19.

Dimethyl [2-(*n*-butylamino)-2-oxoethyl]carbonodithioimidate (9e). IR spectrum, ν, cm^{-1}: 3370 (N–H), 2965, 2928, 2867, 1671 (C=O), 1572 (C=N), 1490, 1451, 1427, 1360, 1317, 1271, 1075, 1028, 1001, 962, 804, 745. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.26 (1H, s, NH); 3.94 (2H, s, CH_2CO); 3.38–3.32 (2H, m, $NHC\underline{H}_2$); 2.58 (3H, s, SCH_3); 2.41 (3H, s, SCH_3); 1.56–1.30 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_3$); 0.94 (3H, t, *J* = 7.3, $(CH_3)_3C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 170.0 (C=O); 162.5 (C=N); 55.2 (C$\underline{H}_2$CO); 38.7 ($NHCH_2$); 31.6 ($CH_2\underline{C}H_2CH_2CH_3$); 20.1 ($(CH_2)_2\underline{C}H_2CH_3$); 14.7 (2$SCH_3$); 13.8 ($(CH_2)_3\underline{C}H_3$). Mass-spectrum, *m*/*z*: 235 [M+H]$^+$. Found, %: C 46.34;

* In compounds **9a**–**h** proton NH is exchangable by D_2O heated at 85°C.

H 7.46; N 11.90; S 27.20. $C_9H_{18}N_2OS_2$. Calculated, %: C 46.12; H 7.74; N 11.95; S 27.36.

Diethyl [2-(*n*-butylamino)-2-oxoethyl]carbonodithioimidate (9f). IR spectrum, ν, cm^{-1}: 3375 (N–H), 2979, 2925, 2854, 1751, 1720, 1680, 1665 (C=O), 1570 (C=N), 1565, 1455, 1448, 1390, 1375, 1263, 1079, 1055, 1028, 752, 724, 690. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.26 (1H, s, NH); 3.95 (2H, s, CH_2CO); 3.37–3.31 (2H, m, $NHC\underline{H}_2$); 3.14–2.96 (4H, m, $2SCH_2$); 1.57–1.30 (10H, m, $2SCH_2C\underline{H}_3$, $CH_2C\underline{H}_2C\underline{H}_2CH_3$); 0.93 (3H, t, *J* = 7.2, $(CH_3)_3C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 170.1 (C=O); 161.4 (C=N); 55.3 ($\underline{C}H_2CO$); 38.7 ($NHCH_2$); 31.7 ($CH_2\underline{C}H_2CH_2CH_3$); 26.5 ($SCH_2$); 25.8 ($SCH_2$); 20.0 ($CH_2CH_2\underline{C}H_2CH_3$); 15.1 ($CH_3$); 13.8 ($CH_3$); 13.7 ($CH_3$). Mass-spectrum, *m*/*z*: 263 $[M+H]^+$. Found, %: C 50.54; H 8.46; N 10.96; S 24.25. $C_{11}H_{22}N_2OS_2$. Calculated, %: C 50.34; H 8.45; N 10.67; S 24.44.

Di(*n*-propyl) [2-(*n*-butylamino)-2-oxoethyl]carbonodithioimidate (9g). IR spectrum, ν, cm^{-1}: 3373 (N–H), 2962, 2923, 2870, 2843, 1752, 1720 (C=O), 1666, 1570 (C=N), 1515, 1455, 1428, 1290, 1154, 1111, 942, 870, 740, 697. ^{1}H NMR spectrum, δ, ppm: 7.26 (1H, s, NH); 3.96 (2H, s, CH_2CO); 3.37–3.32 (2H, m, $NHC\underline{H}_2$); 3.09–2.94 (4H, m, $2SCH_2$); 1.78–1.31 (8H, m, $2SCH_2C\underline{H}_2CH_3$, $CH_2C\underline{H}_2C\underline{H}_2CH_3$); 1.05–0.91 (9H, m, $3CH_3$). ^{13}C NMR spectrum, δ, ppm: 170.2 (C=O); 161.6 (C=N); 55.4 ($\underline{C}H_2CO$); 38.7 ($NHCH_2$); 34.1 (CH_2); 33.5 (CH_2); 31.7 (CH_2); 23.4 (CH_2); 22.2 (CH_2); 20.1 (CH_2); 13.7 (CH_3); 13.6 (CH_3); 13.3 (CH_3). Mass-spectrum, *m*/*z*: 291 $[M+H]^+$. Found, %: C 53.64; H 9.46; N 9.96; S 22.25. $C_{13}H_{26}N_2OS_2$. Calculated, %: C 53.75; H 9.02; N 9.64; S 22.08.

Di(*n*-butyl) [2-(*n*-butylamino)-2-oxoethyl]carbonodithioimidate (9h). IR spectrum, ν, cm^{-1}: 3380 (N–H), 2965, 2920, 2868, 2848, 1745, 1672 (C=O), 1565 (C=N), 1520, 1462, 1435, 1384, 1350, 1319, 1106, 1078, 1031, 867, 804, 730, 695. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.50 (1H, s, NH); 4.03 (2H, s, CH_2CO); 3.36–3.30 (2H, m, $NHC\underline{H}_2$); 3.07 (2H, t, *J* = 7.2, SCH_2); 2.88 (2H, t, *J* = 7.2, SCH_2); 1.71–1.65 (2H, m, CH_2); 1.55–1.49 (4H, m, $2CH_2$); 1.45–1.41 (4H, m, $2CH_2$); 1.28–1.20 (2H, m, CH_2); 1.06–0.99 (3H, m, CH_3); 0.94 (3H, t, *J* = 7.3, CH_3); 0.83 (3H, t, *J* = 7.3, CH_3). ^{13}C NMR spectrum, δ, ppm: 170.1 (C=O); 161.7 (C=N); 55.3 ($\underline{C}H_2CO$); 38.7 ($NHCH_2$); 31.9 (CH_2); 31.6 (CH_2); 31.3 (CH_2); 30.8 ($2CH_2$); 22.2 (CH_2); 21.8 (CH_2); 20.1 (CH_2); 13.7 (CH_3); 13.6 (CH_3); 13.5 (CH_3). Mass-spectrum, *m*/*z*: 319 $[M+H]^+$. Found, %: C 56.64; H 9.46; N 8.96; S 20.05. $C_{15}H_{30}N_2OS_2$. Calculated, %: C 56.56; H 9.49; N 8.79; S 20.13.

Synthesis of compounds 10a–h (General method). Dithioimidate **9a**–**h** (2.0 mmol) was placed in a microwave process vial and irradiated at 150°C for 60 min. The reaction mixture was cooled by air flow. The resulting yellow oil was chromatographed on a silica gel column using EtOAc–hexane, 1:4, as eluent. Compounds **10a**–**h** were obtained in a form of light-yellow oils. The yields are given in Table 1.

3-Benzyl-2-(methylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10a). IR spectrum, ν, cm^{-1}: 3088, 3080, 3035, 2960, 2945, 2858, 2341, 1737, 1732, 1688 (C=O), 1643, 1562 (C=N), 1492, 1455, 1430, 1422, 1344, 1331, 1275, 1171, 1070, 1025, 1017, 974, 881, 727, 701, 655. ^{1}H NMR spectrum, δ, ppm: 7.40–7.24 (5H, m, H Ph); 4.66 (2H, s, $C\underline{H}_2Ph$); 4.19 (2H, s, CH_2CO); 2.51 (3H, s, SCH_3). ^{13}C NMR spectrum, δ, ppm: 180.0 (C=O); 163.9 (C=N); 135.6, 128.7, 128.0, 127.9 (C Ar); 59.0 ($\underline{C}H_2CO$); 44.0 ($\underline{C}H_2Ph$); 12.6 (SCH_3). Mass-spectrum, *m*/*z*: 221 $[M+H]^+$. Found, %: C 60.04; H 5.46; N 12.96; S 14.45. $C_{11}H_{12}N_2OS$. Calculated, %: C 59.98; H 5.49; N 12.72; S 14.56.

3-Benzyl-2-(ethylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10b). IR spectrum, ν, cm^{-1}: 3055, 3032, 2971, 2966, 2930, 2879, 1730 (C=O), 1643, 1605, 1562 (C=N), 1492, 1457, 1420, 1346, 1330, 1265, 1208, 1076, 1057, 1004, 966, 930, 827, 757, 730, 704, 647. ^{1}H NMR spectrum, δ, ppm: 7.38–7.22 (5H, m, H Ph); 4.65 (2H, s, $C\underline{H}_2Ph$); 4.19 (2H, s, CH_2CO); 3.16–3.10 (2H, m, SCH_2); 1.41–1.30 (3H, m, CH_3). ^{13}C NMR spectrum, δ, ppm: 179.9 (C=O); 163.3 (C=N); 135.7, 128.7, 128.0, 127.9 (C Ar); 58.9 ($\underline{C}H_2CO$); 44.0 ($\underline{C}H_2Ph$); 24.8 (SCH_2); 14.2 (CH_3). Mass-spectrum, *m*/*z*: 235 $[M+H]^+$. Found, %: C 61.64; H 6.26; N 11.86; S 13.52. $C_{12}H_{14}N_2OS$. Calculated, %: C 61.51; H 6.02; N 11.96; S 13.68.

3-Benzyl-2-(*n*-propylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10c). IR spectrum, ν, cm^{-1}: 3040, 2977, 2928, 2851, 1671 (C=O), 1663, 1650, 1633, 1628, 1560 (C=N), 1490, 1455, 1427, 1343, 1065, 1018, 877, 655. ^{1}H NMR spectrum, δ, ppm: 7.37–7.22 (5H, m, H Ph); 4.66 (2H, s, $C\underline{H}_2Ph$); 4.17 (2H, s, CH_2CO); 3.13–3.08 (2H, m, SCH_2); 1.77–1.71 (2H, m, $CH_2C\underline{H}_2CH_3$); 1.02–0.98 (3H, m, CH_3). ^{13}C NMR spectrum, δ, ppm: 179.9 (C=O); 163.4 (C=N); 135.6, 128.6, 127.9, 127.8 (C Ar); 58.9 ($\underline{C}H_2CO$); 43.9 ($\underline{C}H_2Ph$); 32.1 (SCH_2); 22.2 ($CH_2\underline{C}H_2CH_3$); 13.3 (CH_3). Mass-spectrum, *m*/*z*: 249 $[M+H]^+$. Found, %: C 62.74; H 6.46; N 11.16; S 12.85. $C_{13}H_{16}N_2OS$. Calculated, %: C 62.87; H 6.49; N 11.28; S 12.91.

3-Benzyl-2-(*n*-butylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10d). IR spectrum, ν, cm^{-1}: 3063, 2968, 2939, 2852, 2362, 2331, 1718 (C=O), 1641, 1575 (C=N), 1499, 1465, 1440, 1388, 1355, 1222, 1167, 1071, 1012, 619. ^{1}H NMR spectrum, δ, ppm: 7.40–7.24 (5H, m, H Ph); 4.64 (2H, s, $C\underline{H}_2Ph$); 4.16 (2H, s, CH_2CO); 3.15–3.10 (2H, m, SCH_2); 1.71–1.65 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 1.45–1.39 (2H, m, $(CH_2)_2C\underline{H}_2CH_3$); 0.95–0.89 (3H, m, CH_3). ^{13}C NMR spectrum, δ, ppm: 179.9 (C=O); 163.3 (C=N); 135.6, 128.6, 127.8, 127.6 (C Ar); 58.8 ($\underline{C}H_2CO$); 43.9 ($\underline{C}H_2Ph$); 30.7 (SCH_2); 29.9 ($CH_2\underline{C}H_2CH_2CH_3$); 21.8 ($(CH_2)_2\underline{C}H_2CH_3$); 13.5 ($CH_3$). Mass-spectrum, *m*/*z*: 263 $[M+H]^+$. Found, %: C 64.14; H 6.96; N 10.76; S 12.25. $C_{14}H_{18}N_2OS$. Calculated, %: C 64.09; H 6.92; N 10.68; S 12.22.

3-(*n*-Butyl)-2-(methylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10e). IR spectrum, ν, cm^{-1}: 2964, 2924, 2866, 1660 (C=O), 1571 (C=N), 1520, 1490, 1450, 1420, 1365, 1312, 1265, 1075, 1040, 1038, 965, 921, 745, 495. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.16 (2H, s, CH_2CO); 3.48–3.40 (2H, m, $C\underline{H}_2(CH_2)_2CH_3$); 2.47 (3H, s, SCH_3); 1.66–1.40 (4H, m, $CH_2(C\underline{H}_2)_2CH_3$); 1.05–0.93 (3H, m, $(CH_2)_3C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 179.9 (C=O); 163.4 (C=N); 58.9 ($\underline{C}H_2CO$); 38.5 ($\underline{C}H_2(CH_2)_2CH_3$); 30.1 ($CH_2\underline{C}H_2CH_2CH_3$); 20.3 ($(CH_2)_2\underline{C}H_2CH_3$); 12.6 ($SCH_3$); 13.7 ($(CH_2)_3\underline{C}H_3$).

Mass-spectrum, *m*/*z*: 187 $[M+H]^+$. Found, %: C 51.64; H 7.46; N 15.06; S 17.25. $C_8H_{14}N_2OS$. Calculated, %: C 51.58; H 7.58; N 15.04; S 17.21.

3-(*n*-Butyl)-2-(ethylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10f). IR spectrum, ν, cm^{-1}: 2978, 2938, 2856, 1742, 1681, 1659 (C=O), 1572 (C=N), 1560, 1515, 1450, 1440, 1395, 1341, 1300, 1175, 1070, 1054, 1018, 937, 742, 720, 692. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.16 (2H, s, CH_2CO); 3.43 (2H, t, *J* = 7.3, $C\underline{H}_2(CH_2)_2CH_3$); 2.99–2.95 (2H, m, SCH_2); 1.64–1.42 (4H, m, $CH_2(C\underline{H}_2)_2CH_3$); 1.40 (3H, t, *J* = 7.3, $SCH_2C\underline{H}_3$); 0.98 (3H, t, *J* = 7.3, $(CH_2)_3C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 179.8 (C=O); 163.2 (C=N); 58.7 ($\underline{C}H_2CO$); 38.4 ($\underline{C}H_2(CH_2)_2CH_3$); 31.7 ($CH_2\underline{C}H_2CH_2CH_3$); 25.5 ($S\underline{C}H_2CH_3$); 20.0 ($(CH_2)_2\underline{C}H_2CH_3$); 14.1 ($SCH_2\underline{C}H_3$); 13.7 ($(CH_2)_3\underline{C}H_3$). Mass-spectrum, *m*/*z*: 201 $[M+H]^+$. Found, %: C 53.84; H 8.26; N 13.96; S 16.15. $C_9H_{16}N_2OS$. Calculated, %: C 53.97; H 8.05; N 13.99; S 16.01.

3-(*n*-Butyl)-2-(*n*-propylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10g). IR spectrum, ν, cm^{-1}: 2933, 2878, 2840, 1739 (C=O), 1579 (C=N), 1520, 1450, 1420, 1395, 1217, 1169, 1119, 1034, 940, 877, 733, 695. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.15 (2H, s, CH_2CO); 3.42 (2H, t, *J* = 7.3, $C\underline{H}_2(CH_2)_2CH_3$); 2.98 (2H, t, *J* = 7.3, SCH_2); 2.02–1.96 (2H, m, $SCH_2C\underline{H}_2CH_3$); 1.62–1.40 (4H, m, $CH_2(C\underline{H}_2)_2CH_3$); 1.06 (3H, t, *J* = 7.2, $S(CH_2)_2C\underline{H}_3$); 0.97 (3H, t, *J* = 7.2, $(CH_2)_3C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 179.8 (C=O); 163.2 (C=N); 58.6 ($\underline{C}H_2CO$); 38.7 ($\underline{C}H_2(CH_2)_2CH_3$); 33.5 ($SCH_2$); 31.7 ($CH_2\underline{C}H_2CH_2CH_3$); 22.2 ($SCH_2\underline{C}H_2CH_3$); 20.1 ($(CH_2)_2\underline{C}H_2CH_3$); 13.7 ($(CH_2)_3\underline{C}H_3$); 13.3 ($S(CH_2)_2\underline{C}H_3$). Mass-spectrum, *m*/*z*: 215 $[M+H]^+$. Found, %: C 56.14; H 8.46; N 13.16; S 14.95. $C_{10}H_{18}N_2OS$. Calculated, %: C 56.04; H 8.47; N 13.07; S 14.96.

3-(*n*-Butyl)-2-(*n*-butylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (10h). IR spectrum, ν, cm^{-1}: 2977, 2953, 2876, 2857, 1748, 1688 (C=O), 1675, 1565 (C=N), 1523, 1466, 1432, 1412, 1388, 1355, 1319, 1276, 1116, 1070, 942, 912, 865, 740, 694. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.14 (2H, s, CH_2CO); 3.40 (2H, t, *J* = 7.3, $C\underline{H}_2(CH_2)_2CH_3$); 2.99–2.95 (2H, m, SCH_2); 2.06–1.33 (8H, m, $2CH_2(C\underline{H}_2)_2CH_3$); 1.02 (3H, t, *J* = 7.3, $S(CH_2)_3C\underline{H}_3$); 0.96 (3H, t, *J* = 7.3, $N(CH_2)_3C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 179.7 (C=O); 163.1 (C=N); 58.6 ($\underline{C}H_2CO$); 38.7 ($\underline{C}H_2(CH_2)_2CH_3$); 30.3 ($SCH_2$); 29.8 ($CH_2$); 29.5 ($CH_2$); 27.8 ($CH_2$); 20.1 ($CH_2$); 13.7 ($N(CH_2)_3\underline{C}H_3$); 13.4 ($S(CH_2)_3\underline{C}H_3$). Mass-spectrum, *m*/*z*: 229 $[M+H]^+$. Found, %: C 57.84; H 8.76; N 12.16; S 14.15. $C_{11}H_{20}N_2OS$. Calculated, %: C 57.86; H 8.83; N 12.27; S 14.04.

Supplementary information file containing NMR spectral data of compounds **8b**, **9a**–**d**, **10a**–**d** is available at the journal website at http://link.springer.com/journal/10593.

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