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The Invention of Radical Reactions. Part XXVI. New Thio- and Seleno-Hydroxamic Acids; Radical Chemistry of their *O*-Acyl Derivatives.

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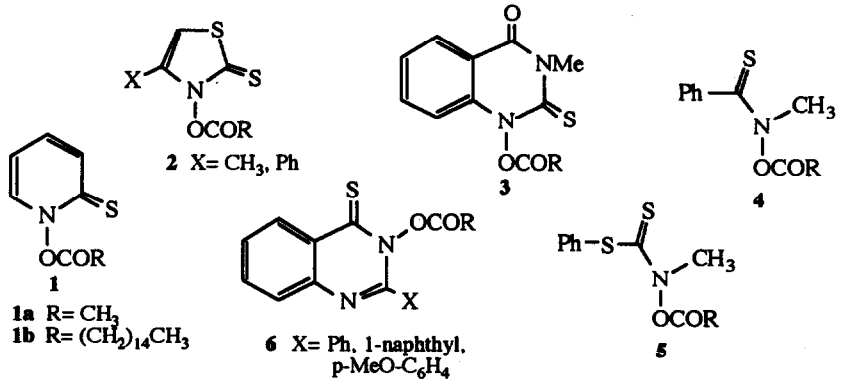
Abstract: *New thio- and seleno-hydroxamic acids have been synthesized from various 4,4 -disubstituted thiazolidine-2,5-dithiones. Their corresponding O-acyl derivatives rearrange photochemically, with visible light, in an identical manner to the acyl derivatives of N-hydroxy-2-thiopyridone. A wide range of half-lives was observed.*

Over the past ten years, *O*-acyl derivatives of *N*-hydroxy-2-thiopyridone **1** have been extensively used as a mild and convenient source of carbon radicals[1] which have been trapped in a variety of ways[2]. This type of compound was also used for the controlled generation of nitrogen[3] as well as oxygen-centered radicals[4]. Recently, a new and simple procedure for the formation of carbon radicals has been developed, which is based upon a radical exchange reaction between the methyl radical, generated from the photolysis of the *O*-acetyl **1a**, and organo-telluride derivatives[5]. The efficiency, mildness and stereoselectivity[6] observed in these radical processes have found successful applications in the synthesis of natural products[5bc,7].

More recently, we have demonstrated that **1a** could be used as an efficient substitute for tin hydride in the modified Julia olefin synthesis by radical deoxygenation of xanthate derivatives of β-hydroxysulfones[8].

The radical chemistry of some known thiohydroxamic acids has been previously studied. While the bright yellow *O*-acyl derivatives of **1** decompose smoothly when photolysed with visible light, compounds **2**, **3**, **4** and **5** are essentially colorless and require the use of a UV lamp[9]. In contrast compounds of type **6**, which have been studied recently[10], were found to decompose very rapidly when photolysed with a tungsten lamp.



Yamamoto *et al.*[11] have reported an efficient synthesis of thiazolidine 2,5-dithiones obtained by reacting an α-metallated arylalkyl isothiocyanate with carbon disulfide. The known compound **9a**, prepared via **7a** and **8a**, was converted into the thiohydroxamic acid **10a**, in 73% yield, by treatment with hydroxylamine hydrochloride and pyridine in refluxing ethanol (Scheme 1). This yellow crystalline compound is thermally and photochemically stable. Acylation of **10a** with palmitoyl chloride and pyridine in ether, at -20°C for 30 min, afforded the pale yellow *O*-palmitoyl derivative **11a** in almost quantitative yield. If the reaction was carried at higher temperature, a mixture of the *S*-acyl and *O*-acyl derivatives was obtained.

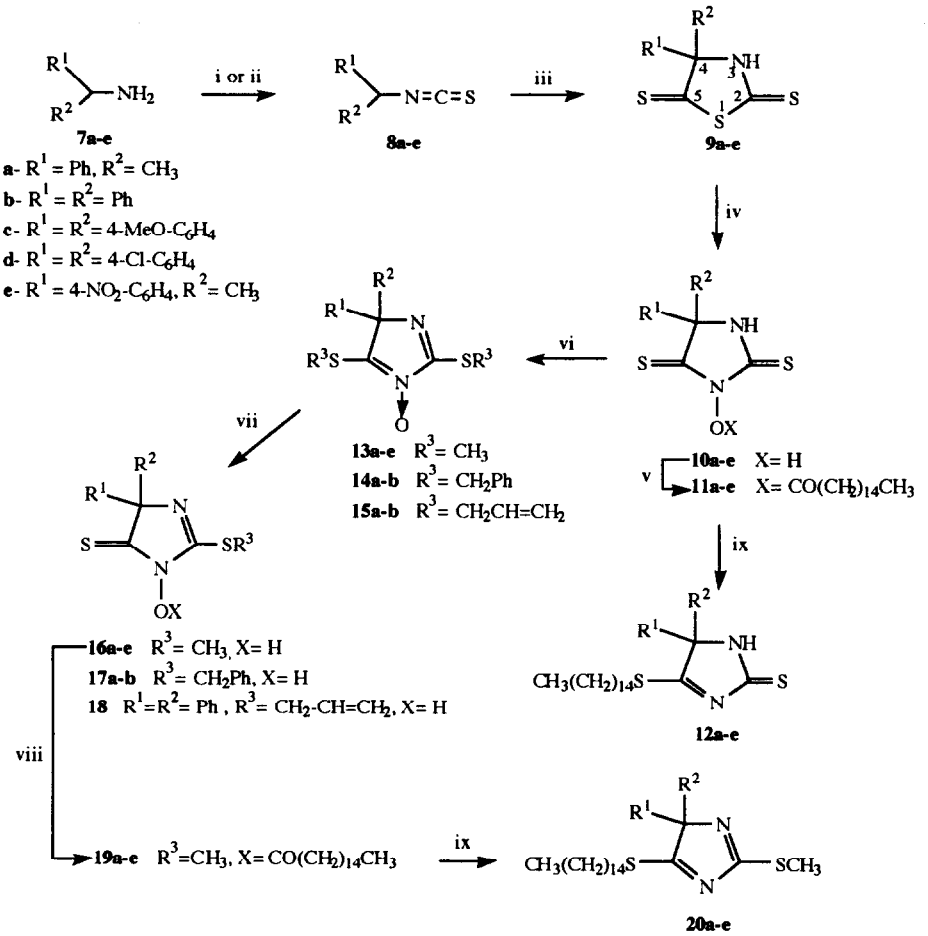
On the other hand, treatment of **10a** with methyl iodide and triethylamine, in dichloromethane at room temperature, afforded the *N*-oxide **13a**. This reaction gave exclusively the dialkylated product. The attempted formation of the desired **16a** by a regioselective monomethylation of the thioamide group was unsuccessful. Nevertheless, **13a** could be transformed easily into **16a** by reacting the *N*-oxide with sodium hydrosulfide in DMF at room temperature. This thiohydroxamic acid was obtained in 79% yield and is stable at room temperature when protected from light. Acylation of **16a** with palmitoylchloride and pyridine, in dichloromethane at 0°C, afforded the pale yellow *O*-palmitoyl derivative **19a**.

With these two *O*-acyl derivatives **11a** and **19a** in hand, attention was given to their radical decarboxylative rearrangement. Thus, their photolysis with tungsten light was carried out in $CDCl_3$ at 0°C under the same conditions of irradiation and concentration (see experimental). Compound **1b** was subjected to an identical photolytic procedure.

The disappearance of the *O*-palmitoyl derivatives was followed by NMR and the half-lives were determined. The yield of rearranged product was also calculated by NMR after completion of the reaction. The results are displayed in Table 1 (entries 1, 2 and 7).

The differences in the half-life values show that **11a** rearranged slowly compared to **1b** and in contrast **19a** is more light sensitive than the thiopyridone derivative. The colorless imidazole **20a** was obtained in almost quantitative yield, after only 1 min of photolysis. In the case of the dihydroimidazole structure, the reaction stopped after 6 min to give a moderate yield of **12a** (60%) and the remaining **11a**. **12a** is a bright yellow

compound which could interfere in the radical process as its concentration increases during the reaction. To have a proof of its structure **12a** was transformed to **20a** by simple methylation of the thioamide group, using methyl iodide and triethylamine in dichloromethane.



a- R^1 = Ph, R^2= CH_3
b- R^1 = R^2= Ph
c- R^1 = R^2= 4-MeO-C_6H_4
d- R^1 = R^2= 4-Cl-C_6H_4
e- R^1 = 4-NO_2-C_6H_4, R^2= CH_3

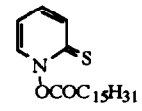
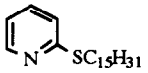
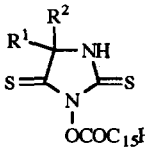
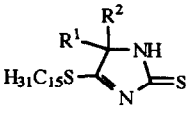
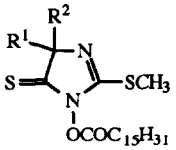
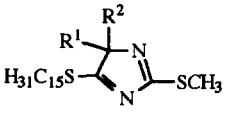
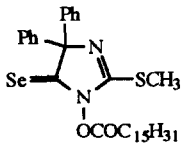
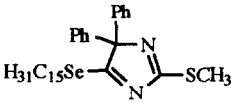
i- CS_2, DCC, Et_2O or THF, -10°C 3hrs, r.t. 12hrs; **ii-** CS_2, Et_3N, DCC, Py, -10°C 1hr, r.t. 1hr; **iii-** $tBuO^-K$, CS_2, THF, -78°C to r.t. 12 hrs; **iv-** $NH_2OH.HCl$, Py, EtOH, reflux, 5 hrs; **v-** $ClCOC_{15}H_{31}$, Py, Et_2O, -20°C, 30 min; **vi-** Et_3N, CH_3I or $PhCH_2Br$ or CH_2=$CHCH_2Br$, CH_2Cl_2, r.t.; **vii-** NaSH, DMF, r.t, 1hr; **viii-** $ClCOC_{15}H_{31}$, Py, CH_2Cl_2, 0°C, 30 min; **ix-** hv , $CDCl_3$, 0°C.

Scheme 1

It was clear that we had in our hand two interesting thiohydroxamic structures, easily obtained from the same 5-membered ring, which underwent radical decarboxylation under the same conditions of photolysis with different rates of reaction.

We next investigated other derivatives of these two structures and prepared some new 4,4 -disubstituted thiazolidine 2,5-dithiones **9c-e** as well as the known **9b**, starting from the corresponding arylamine **7**. Benzhydrylamine **7b**, as well as phenylethylamine **7a**, are commercially available. Di-p-anisylmethylamine **7c** was prepared from p-dimethoxybenzophenone[12]. Dichlorobenzhydrylamine **7d** was obtained by reduction of the corresponding oxime, using lithium aluminum hydride as reducting agent, according to the Cram and Guthrie procedure[13]. p-Nitrophenylethylamine **7e** was obtained by nitration of N-acetyl-phenylethylamine using the procedure described by Baumgarten and Petersen[14]. The isothiocyanates **8a-e** were prepared using two different methods reported by Jochims[15]. The first consists of reacting the amine with carbon disulfide and DCC, in ether or THF, and gave excellent yields of isothiocyanates **8a-c**. Use of the second procedure was required for the preparation of **8d-e** due to the low nucleophilic character of the starting amines **7d-e**. This method consists in preparing first the triethylamonium salt of the carbamate intermediate and then reacting this salt with DCC in pyridine at room temperature.

Table 1: Half-Lives[a] of Acyl Derivatives **1, 11, 19, 22** and yields[b] of their rearranged products

entries	*O*-palmitoyl derivatives		$t_{1/2}$ (sec)	rearranged products		yield (%)
1		**1b**	175			50
2		**11a**	250		**12a**	60
3		**11b**	100		**12b**	72
4		**11c**	170		**12c**	68
5		**11d**	140		**12d**	62
6		**11e**	275		**12e**	55
7		**19a**	25		**20a**	97
8		**19b**	15		**20b**	95
9		**19c**	26		**20c**	96
10		**19d**	23		**20d**	97
11		**19e**	50		**20e**	95
12		**22**	<5		**23**	100

[a] Determined in 0.1M $CDCl_3$ solutions. Photolysis: tungsten light (270 W), 0°C.

[b] Calculated by 200 MHz ^1H NMR with an internal reference.

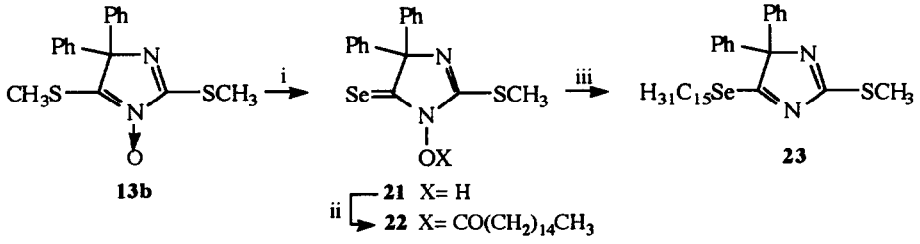
The thiohydroxamic acids **10b-e** and **16b-e**, as well as their palmitoyl derivatives **11b-e** and **19b-e** were prepared following the same sequence of reactions previously described (Scheme 1). It was of interest to investigate the effect of the substituents at the C-4 position of these two types of structure. Compounds **11b-e** and **19b-e** upon irradiation gave respectively their rearranged products **12b-e** and **20b-e**.

Comparison of the half-life values between these two types of structure showed that the imidazolidines **11** are 5 to 10 times less reactive than the dihydroimidazoles **19**. Also the yields of **20** are consistently better than those of **12**. This is in keeping with the distribution of electron density on the N-OCO- group over two thiocarbonyl functions. In the case of **19** this cross resonance does not pertain and normal acylthiohydroxamic chemistry is seen. Furthermore, in each of the categories we observed a difference in the half-life values depending on the substitution at the C-4 position. For example, the 4,4-diphenyl derivatives **11b** and **19b** (Table 1, entries 3 and 8) decompose approximately three times faster than their corresponding p-nitrophenyl derivatives **11e** and **19e** (Table 1, entries 6 and 11).

We also prepared some other derivatives such as the thiohydroxamic acids **17** and **18** (Scheme 1). However, these compounds were not stable enough for further manipulation.

Few seleno-hydroxamic acids have been reported. However *N*-hydroxy-2-selenopyridone was described some time ago[16]. We later showed that this was a useful reagent for the synthesis of L-vinylglycine[17]. The selenocarbonyl function captured carbon radicals more efficiently than any other trap. However, *N*-hydroxy-2-selenopyridone was easily oxidized by air to the corresponding di-selenide.

We decided to see if methylthio-*N*-oxides like **13b** could afford a selenohydroxamic acid **21** by treatment with sodium hydrogen selenide. In the event **21** was formed in good (91%) yield as an orange stable solid (Scheme 2). Its palmitoyl derivative **22** on irradiation rearranged very rapidly ($t_{1/2} < 5$ sec) to give a quantitative yield of **23** (Table 1, entry 12).



i- NaSeH, EtOH, 0°C, 1 hr; ii- $ClCOC_{15}H_{31}$, Et_2O, - 20°C, 30 min; iii- hv , $CDCl_3$, 0°C.

Scheme 2

In conclusion, we have synthesized a number of new thio- and seleno-hydroxamic acids. The compounds of type **19** are of excellent photosensitivity. In particular **19b**, based on **16b**, has excellent photochemical properties. If *N*-Hydroxy-2-thiopyridone were not an inexpensive reagent (from the Olin Corporation) then the easily prepared diphenyl derivative **16b** would make an excellent substitute. Most of the new compounds that we describe are easily prepared on a large scale and can be stored without decomposition at room temperature in the dark.

Experimental

Melting points were determined with a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 spectrophotometer. ^1H and ^{13}C NMR spectra were measured with a Varian Gemini 200 or a Varian XL 200E. Chemical Shifts are in p.p.m. downfield from tetramethylsilane used as an internal standard (δ values). Mass spectra were obtained on a V.G. Analytical 70s high-resolution double-focusing magnetic sector mass spectrometer with attached VG 11/250J data system in the EI mode. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Solvents were used either as purchased or dried and purified by standard methods. All the reactions were effected under an inert atmosphere of argon. Flash Chromatography was performed using Kiesegel 60 (230-400 mesh, E. Merck). Phenylethylamine and benzhydrylamine were purchased from the Aldrich Chemical Co., Inc.

Preparation of isothiocyanates (8a-e):

1-Phenylethylisothiocyanate ***8a***[18]. To a solution of phenylethylamine (10 ml, 7.75 mmol) in dry ether (100 ml) were added, at - 10°C, CS_2 (30 ml) and DCC (16 g, 7.75 mmol). The reaction mixture was allowed to warm slowly to room temperature during a period of 3 hrs and stirred for a further 12 hrs at room temperature. The thiourea which has precipitated was filtered and the solvent removed under vacuum. The residue was taken up in ether and more of thiourea was filtered. Evaporation of the solvent and rapid filtration on silica gel (hexane) gave the isothiocyanate (11 g, 90 %) as a liquid. IR (CH_2Cl_2,cm^{-1}) 2093; ^1H NMR ($CDCl_3$) 1.6 (3H, d), 4.9 (1H, q), 7.35 (5H, m); ^{13}C NMR ($CDCl_3$) 24.9 (CH_3), 57 (CH), 125.3 (CH), 128.1 (CH), 128.8 (CH), 140 (Cq).

1,1-Diphenylmethylisothiocyanate ***8b***. This compound was prepared in 92% yield from **7b** in a manner analogous to **8a** and was isolated as a colorless solid; m.p. 58 °C {lit.[19]: 60 °C}; IR (CH_2Cl_2,cm^{-1}) 2077; ^1H NMR ($CDCl_3$) 6.0 (1H, s), 7.36 (10H, s); ^{13}C NMR ($CDCl_3$) 64.5 (CH), 126.5 (CH), 128.2 (CH), 128.9 (CH), 139.1 (Cq).

1,1-Di-p-anisylmethylisothiocyanate ***8c***. This compound was prepared from **7c** in a manner analogous to that used for **8a** with the difference that the reaction was carried out in THF. It was obtained (72%) as a pale yellow solid, m.p. 47 °C {lit.[19]: 48 °C}; IR (CH_2Cl_2,cm^{-1}) 2073, 1507, 1174, 1030; ^1H NMR ($CDCl_3$) 3.7 (6H, s); 5.9 (1H, s); 6.88 (4H, d); 7.2 (4H, d); ^{13}C NMR ($CDCl_3$) 55.4 (OCH_3), 63.6 (CH), 114.1 (CH), 127.7 (CH), 131.5 (Cq), 159.3 (Cq).

Di-p-chlorobenzhydrylisothiocyanate ***8d***. To a solution of pyridine (1 ml) and CS_2 (2 ml) was added, at -10°C, Et_3N (0.55 ml, 3.97 mmol). To this mixture was added slowly a solution of **7d** (1g, 3.97 mmol) in pyridine (2 ml) and the reaction was stirred for 1hr at -10°C. DCC (819 mg, 3.97 mmol) in solution in pyridine (2 ml) was added slowly at -10°C and the reaction mixture was stirred 1hr at -10°C and then for a further 1hr at room temperature. The solvents were evaporated and the residue was taken up in ether. The thiourea, which had precipitated, was filtered and the solvent evaporated under reduced pressure. After flash chromatography of the residue on silica gel (hexane) and recrystallization (ether-hexane), the isothiocyanate (0.91 g, 78%) was obtained as a colorless compound. m.p. 82-83 °C {lit.[19]: 85 °C}; ^1H NMR ($CDCl_3$) 5.92 (1H, s); 7.20 (4H, d); 7.34 (4H, d); IR (CH_2Cl_2, cm^{-1}) 2063, 1089; ^{13}C NMR ($CDCl_3$) 63.3 (CH), 127.8 (CH), 129.2 (CH), 134.4 (Cq), 137.3 (Cq).

*1-p-Nitrophenylethylisothiocyanate **8e***. This compound was prepared from **7e** in a manner analogous to that of **8d**, and was obtained as a yellow liquid (71%). IR (CH_2Cl_2, cm^{-1}) 2091, 1525, 1348 ; ^1H NMR ($CDCl_3$) 1.82 (3H, d, J=7Hz), 5.1 (1H, q), 7.52 (2H, d, J=8.8Hz), 8.25 (2H, d, J=8.8Hz); MS (EI, m/z): 208 $(M)^+$, 150 (M-NCS)$^+$, 104 (150- $NO_2)^+$.

Preparation of 4,4-Disubstituted Thiazolidine-2,5-dithiones (9a-b):

*4-Methyl-4-phenylthiazolidine-2,5-dithione **9a***:. In a typical experiment: to a stirred solution of potassium t-butoxide (7.99 g, 1.1 eq) in dry THF, cooled to -78°C, was added dropwise, over a period of 1 hr and under argon, a mixture of 1-phenylethylisothiocyanate **8a** (10.56 g, 64.78 mmoles) and CS_2 (5.8 ml, 1.5 eq). After the addition was complete , the reaction mixture was stirred for a further 30 min at -78°C, then for 16 hrs at room temperature. The solution was diluted with ether and washed with water. The aqueous layer was acidified with 6N HCl and re-extracted into ether. The organic layers were combined and dried over $MgSO_4$, filtered and evaporated under reduced pressure to give after crystallization the pure thiazolidinedithione **9a** (10 g, 65%) as orange crystals, m.p. 100-102 °C (benzene/ hexane) {lit.[11] m.p. 114 °C}; ^1H NMR ($CDCl_3$) 2.07 (3H, s), 7.4 (5H, m), 9.4 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 28 (CH_3), 87.7 (C-Ph), 125.4 (CH), 129.1 (CH), 129.2 (CH), 139.4 (Cq), 160 (Cq), 193.5 (C=S), 235.6 (C=S).

*4,4-Diphenylthiazodine-2,5-dithione **9b***. This formed red crystals (85%), m.p. 218-220 °C (EtOH) {lit.[11] 225-226 °C}; ^1H NMR ($(CD_3)_2SO$) 7.4 (10H, m), 12.6 (1H, NH, s); ^{13}C NMR ($(CD_3)_2SO$) 94.2 (C-Ph), 127.7 (CH), 128.7 (CH), 128.9 (CH), 139.7 (Cq), 190 (C=S), 236.7 (C=S).

*4,4-Di-p-anisylthiazolidine-2,5-dithione **9c***: This was a red crystalline compound (92%), m.p.139 °C (ether - hexane); ^1H NMR ($CDCl_3$) 3.8 (6H, s), 6.86 (4H, d), 7.28 (4H, d), 9.25 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 55.3 (OCH_3), 93.1 (C-(p-MeO-$C_6H_4)_2$), 114.1 (CH), 129.2 (CH), 131.7 (Cq), 160 (Cq), 192.4 (C=S), 234.5 (C=S); Anal. Calcd for $C_{17}H_{15}NO_2S_3$: C, 56.48; H, 4.18; N, 3.87; S, 26.61 Found: C, 56.57; H, 4.17; N, 3.88; S, 26.55.

*4,4-Di-p-chlorophenylthiazolidine-2,5-dithione **9d***. This was a red crystalline compound (78%); m.p. 224 °C (dichloromethane - ethanol); ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 7.4 (8H, m), 12.5 (1H, NH, s); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 92.5 (C-(p-Cl-$C_6H_4)_2$), 128.2 (CH), 129.1 (CH), 134.1 (Cq), 138 (Cq), 190.3 (C=S), 234.6 (C=S), Anal. Calcd for $C_{15}H_9Cl_2NS_3$: C, 48.64; H, 2.45; N, 3.78; S, 25.97 Found: C, 48.68; H, 2.47; N, 3.79; S, 25.95.

*4-Methyl-4-p-nitrophenylthiazolidine-2,5-dithione **9e***: This compound was obtained as orange needles (57%); m.p. 147 °C (dichloromethane - hexane); ^1H NMR ($CDCl_3$) 2.15 (3H, s), 7.65 (2H, d, J=9Hz), 8.25 (2H, d, J=9Hz), 8.93 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 28.4 (CH_3), 86.6 (C-CH_3), 124.2 (CH), 126.7 (CH), 145.7 (Cq), 148.1 (Cq), 193.7 (C=S), 233.4 (C=S), Anal. Calcd for $C_{10}H_8N_2O_2S_3$: C, 42.23; H, 2.83; N, 9.85; S, 33.82 Found: C, 42.33; H, 2.87; N, 9.78; S, 33.75.

Preparation of 4,4-Disubstituted-1-hydroxy-imidazolidine-2,5-dithiones (10a-e):

*1-Hydroxy-4-methyl-4-phenyl-imidazolidine-2,5-dithione **10a**.* In a typical experiment: to a solution of **9a** (10 g, 41.84 mmol), in ethanol (20 ml) was added hydroxylamine hydrochloride (3.5 g, 1.2 eq) and pyridine (10.2 ml, 3 eq). The solution was refluxed for 5 hrs and the solvent was then removed under vacuum. The residue was diluted with dichloromethane and washed with dilute aqueous potassium carbonate. The aqueous layer was separated, washed twice with dichloromethane, then acidified with 6N HCl and re-extracted into dichloromethane. The organic layer was dried over $MgSO_4$, filtered and evaporated under vacuum to give, after crystallization, the pure thiohydroxamic acid **10a** (7.3 g, 73%) as a yellow crystalline compound; m.p. 124 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 3412, 3189, 1493, 1445, 1296, 1208, 1125; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 1.88 (3H, s), 7.4 (5H, m), 11.2 (1H, NH, s), 11.6 (1H, OH, br); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 26.4 (CH_3), 72.7 (C-Ph), 125.4 (CH), 128 (CH), 128.2 (CH), 139.2 (Cq), 178.3 (C=S), 198.5 (C=S); MS (EI, m/z): 238 $(M)^+$, 222 $(M-O)^+$, 162 $(MH-HONCS)^+$; Anal. Calcd for $C_{10}H_{10}N_2OS_2$: C, 50.39; H, 4.23; N, 11.75; S, 26.90 Found: C, 50.38; H, 4.24; N, 11.72; S, 26.99.

*1-Hydroxy-4,4-diphenylimidazolidine-2,5-dithione **10b**.* This was a yellow crystalline compound (78%), m.p. 148-150 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 3405, 3159, 1490, 1443, 1295, 1218, 1164, 1124; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 7.38 (10H, s), 11.8 (1H, NH, s), 12 (1H, OH, s); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 78.7 (C-Ph), 127.5 (CH), 128 (CH), 128.2 (CH), 139.5 (Cq), 177.3 (C=S), 195.5 (C=S); MS (EI, m/z): 300 $(M)^+$, 284 $(M-O)^+$, 252 $(284-S)^+$; Anal. Calcd for $C_{15}H_{12}N_2OS_2$: C, 59.97; H, 4.02; N, 9.32; S, 21.35 Found: C, 59.91; H, 4.05; N, 9.37; S, 21.25.

*1-Hydroxy-4,4-di-p-anisylimidazolidine-2,5-dithione **10c**.* This was obtained as a yellow solid (87%), m.p. 93 °C ; IR (CH_2Cl_2, cm^{-1}) 3406, 3171, 1498, 1445, 1294, 1177, 1166; ^1H NMR ($CDCl_3$) 3.75 (6H, s), 6.8 (4H, d), 7.2 (4H, d), 8.82 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 55.3 (OCH_3), 79.6 (C-(p-MeO-$C_6H_4)_2$), 114 (CH), 128.9 (CH), 130.6 (Cq), 159.8 (Cq), 174.6 (C=S), 192.1 (C=S); Anal. Calcd for $C_{17}H_{16}N_2O_3S_2$: C, 56.64; H, 4.47; N, 7.77; S, 17.79 Found: C, 56.53; H, 4.42; N, 7.73; S, 17.88.

*1-Hydroxy-4,4-di-p-chlorophenylimidazolidine-2,5-dithione **10d**.* This was a yellow crystalline compound (85%), m.p. 181 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3398, 3181, 1488, 1440, 1295, 1247, 1167, 1094, 1012, 826; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 7.3 (8H, m), 11.05 (2H, NH, s, OH, br); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 78 (C-(p-Cl-$C_6H_4)_2$), 128.3 (CH), 129.1 (CH), 134.5 (Cq), 137.8 (Cq), 177.4 (C=S), 193.8 (C=S); Anal. Calcd for $C_{15}H_{10}Cl_2N_2OS_2$: C, 48.78; H, 2.73; N, 7.58; S, 17.36 Found: C, 48.89; H, 2.76; N, 7.55; S, 17.42

*1-Hydroxy-4-methyl-4-p-nitrophenylimidazolidine-2,5-dithione **10e**.* This was a yellow crystalline compound (70%), m.p. 130-132 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 3405, 3176, 1507, 1347, 1288, 1208, 1091, 853; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 1.89 (3H, s), 7.7 (2H, d), 8.25 (2H, d), 11.5 (1H, NH, s), 11.9 (1H, OH, s); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 27 (CH_3), 72 (C-CH_3), 123.2 (CH), 126.9 (CH), 145.9 (Cq), 147.1 (Cq), 178.4 (C=S), 196.9 (C=S); MS (EI, m/z): 283 $(M)^+$, 267 $(M-O)^+$; Anal. Calcd for $C_{10}H_9N_3O_3S_2$: C, 42.39; H, 3.20; N, 14.83; S, 22.63 Found: C, 42.48; H, 3.22; N, 14.89; S, 22.54.

Preparation of 4,4-Disubstituted-2,5-Dialkylthio-(4H)-imidazole-1-oxides (13,14,15):

General procedure for the preparation of **13a-e**: to a cooled solution of thiohydroxamic acid **10a-e** (1 mmol) in dichloromethane (5 ml) was added successively Et_3N (2.5 mmol) and MeI (2.5 mmol). After 30 min at 0 °C, the reaction mixture was stirred for a further 8 hrs at room temperature. The solution was then diluted with dichloromethane and washed with water. The organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduce pressure. Flash chromatography of the residue on silica gel (ether-hexane 1:1) gave the pure N-oxide **13a-e**.

2,5-Dimethylthio-4-methyl-4-phenyl-(4H)-imidazole-1-oxide ***13a.*** This was a colorless crystalline compound (72 %), m.p. 90-92 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 1596, 1490, 1418, 1249, 1126, 893; ^1H NMR ($CDCl_3$) 1.86 (3H, s), 2.55 (3H, s), 2.65 (3H, s), 7.3 (5H, m); ^{13}C NMR ($CDCl_3$) 11.9 (SCH_3), 13.4 (SCH_3), 23.4 (CH_3), 81 (C-Ph), 125.6 (CH), 128.5 (CH), 128.8 (CH), 136.6 (Cq), 160.3 (Cq), 168.9 (Cq); MS (EI, m/z): 266 $(M)^+$, 250 $(M- O)^+$, 220 $(M- HSMe)^+$, 163 $(MePhCHCSMe)^+$; Anal. Calcd for $C_{12}H_{14}N_2OS_2$: C, 54.10; H, 5.29; N, 10.51; S, 24.07 Found: C, 54.26; H, 5.33; N, 10.59; S, 23.96.

2,5-Dimethylthio-4,4-diphenyl-(4H)-imidazole-1-oxide ***13b.*** This was obtained as a colorless crystalline compound (77%), m.p. 146 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 1598, 1486, 1140, 1116; ^1H NMR ($CDCl_3$) 2.5 (3H, s), 2.59 (3H, s), 7.28 (10H, m); ^{13}C NMR ($CDCl_3$) 12.3 (SCH_3), 13.3 (SCH_3), 87.4 (C-Ph_2), 127.7 (CH), 128.4 (CH), 128.5 (CH), 138.3 (Cq), 156.1 (Cq), 169.1 (Cq); MS (EI, m/z): 328 $(M)^+$, 312 $(M- O)^+$, 282 $(MH- HSMe)^+$, 225 $(282- NC=NOH)^+$; Anal. Calcd for $C_{17}H_{16}N_2OS_2$: C, 62.16; H, 4.91; N, 8.53; S, 19.52 Found: C, 62.23; H, 4.94; N, 8.58; S, 19.61.

2,5-Dimethylthio-4,4-di-p-anisyl-(4H)-imidazole-1-oxide ***13c.*** This compound formed colorless crystals (78%), m.p. 149 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 1599, 1486, 1176, 1031, 830; ^1H NMR ($CDCl_3$) 2.56 (3H, s), 2.65 (3H, s), 3.8 (6H, s), 6.86 (4H, d), 7.2 (4H, d); ^{13}C NMR ($CDCl_3$) 12.2 (SCH_3), 13.2 (SCH_3), 55.1 (OCH_3), 86.6 (C-(p-MeO-$C_6H_4)_2$), 113.7 (CH), 128.8 (CH), 130.1 (Cq), 156.6 (Cq), 159.4 (Cq), 168.5 (Cq); MS (EI, m/z): 388 $(M)^+$, 372 $(M- O)^+$, 342 $(MH- HSMe)^+$, 285 $(342- NC=NOH)^+$; Anal. Calcd for $C_{19}H_{20}N_2O_3S_2$: C, 58.73; H, 5.19; N, 7.21; S, 16.50. Found: C, 58.63; H, 5.18; N, 7.20; S, 16.44.

2,5-Dimethylthio-4,4-di-p-chlorophenyl-(4H)-imidazole-1-oxide ***13d.*** This compound formed colorless crystals (83%), m.p. 128 °C (dichloromethane - hexane) recrystallized with $(H_2O)_{0.5}$; IR (CH_2Cl_2, cm^{-1}) 1596, 1482, 1115, 1093, 826; ^1H NMR ($CDCl_3$) 1.85 (1H, H_2O), 2.6 (3H, s), 2.73 (3H, s), 7.2 (4H, d), 7.35 (4H, d); ^{13}C NMR ($CDCl_3$) 12.4 (SCH_3), 13.3 (SCH_3), 86.2 (C-(p-Cl-$C_6H_4)_2$), 128.8 (CH), 129 (CH), 134.7 (Cq), 136.7 (Cq), 154.8 (Cq), 170 (Cq); MS (EI, m/z): 396 $(M)^+$, 380 $(M- O)^+$, 350 $(MH- HSMe)^+$, 293 $(350- NC=NOH)^+$; Anal. Calcd for $C_{17}H_{14}Cl_2N_2OS_2(H_2O)_{0.5}$: C, 50.24; H, 3.69; N, 6.89; S, 15.78. Found: C, 50.34; H, 3.69; N, 6.86; S, 15.79.

2,5-Dimethylthio-4-methyl-4-p-nitrophenyl-(4H)-imidazole-1-oxide ***13e.*** This was a pale yellow crystalline compound (66%), m.p. 151 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 1728, 1593, 1516, 1488, 1344, 1120, 851; ^1H NMR ($CDCl_3$) 1.89 (3H, s), 2.59 (3H, s), 2.76 (3H, s), 7.52 (2H, d, J=9Hz), 8.22 (2H, d, J=9Hz); ^{13}C NMR ($CDCl_3$) 12 (SCH_3), 13.3 (SCH_3), 24.3 (CH_3), 80 (C-Ph), 123.9 (CH), 126.9 (CH), 144.5

(Cq), 147.7 (Cq), 156.4 (Cq), 170.7 (Cq); MS (EI, m/z): 311 $(M)^+$, 208 $(M- N=(NO)SCH_3)^+$; Anal. Calcd for $C_{12}H_{13}N_3O_3S_2$: C, 46.28; H, 4.21; N, 13.49; S, 20.59 Found: C, 46.35; H, 4.23; N, 13.44; S, 20.65.

2,5-Dibenzylthio-4-methyl-4-phenyl-(4H)-imidazole-1-oxide ***14a.*** To a cooled solution of **10a** (2 g, 8.4 mmol) in dichloromethane (30 ml) was added successively Et_3N (0.8 ml, 2.1 eq) and benzylbromide (2.1 ml, 2.1 eq). The reaction mixture was stirred for 4 hrs at room temperature then washed with dilute $NaHCO_3$ and water. After drying over $MgSO_4$, filtration and evaporation, crystallization from ether - hexane afforded 1.3 g of **14a** and chromatography of the mother liquor on silica gel (ether - hexane 1:1) gave 320 mg more N-Oxide. This compound formed colorless crystals (46%); m.p. 114 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 1596, 1489, 1121; ^1H NMR ($CDCl_3$) 1.38 (3H, s), 4.38 (1H, s and 2H, d, J=12Hz), 4.95 (1H, d, J=12.7Hz), 7 to 7.5 (15H, m); ^{13}C NMR ($CDCl_3$) 23.9 (CH_3), 32.5 (SCH_2), 35 (SCH_2), 80.9 (C-Ph), 125.5 to 129.1 (CH), 135.7 (Cq), 136.8 (Cq), 137 (Cq), 156.5 (Cq), 168 (Cq); MS (EI, m/z): 418 $(M)^+$, 402 $(M- O)^+$, 311 $(402- CH_2Ph)^+$; Anal. Calcd for $C_{24}H_{22}N_2OS_2$: C, 68.86; H, 5.30; N, 6.69; S, 15.32 Found: C, 69.14; H, 5.44; N, 6.62; S, 15.21.

2,5-Dibenzylthio-4,4-diphenyl-(4H)-imidazole-1-oxide ***14b.*** This compound was prepared from **10b** in a manner analogous to that used for the preparation of **14a**. This formed colorless crystals (61%), m.p. 106 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 1597, 1483, 1134, 1108; ^1H NMR ($CDCl_3$) 4.34 (2H, s), 4.71 (2H, s), 7 (4H, m), 7.1 to 7.3 (14H, m), 7.9 (2H, m); ^{13}C NMR ($CDCl_3$) 33.2 (SCH_2), 35 (SCH_2), 87.5 (C-Ph_2), 127.5 to 129.2 (CH), 135.7 (Cq), 136.2 (Cq), 138.6 (Cq), 154.5 (Cq), 167.9 (Cq); MS (EI, m/z): 480 $(M)^+$, 464 $(M-O)^+$, 373 $(464- CH_2Ph)^+$; Anal. Calcd for $C_{29}H_{24}N_2OS_2$: C, 72.46; H, 5.03; N, 5.83; S, 13.34 Found: C, 72.54; H, 5.06; N, 5.87; S, 13.34.

2,5-Diallylthio-4-methyl-4-phenyl-(4H)-imidazole-1-oxide ***15a.*** To a cooled solution of **10a** (2.5 g, 10.5 mmol) in dichloromethane (30 ml) were added Et_3N (3.66 ml, 2.5 eq) and allyl bromide (2.27 ml, 2.5 eq). The reaction mixture was stirred for 3 hrs at room temperature then washed with dilute $NaHCO_3$ and water. After being dried over $MgSO_4$, filtered and evaporated, the residue was chromatographed on silica gel (ether - hexane 2:8) to give 1.28 g of **15a**. This compound formed colorless crystals (38%), m.p. 51 °C (hexane); IR (CH_2Cl_2, cm^{-1}) 1597, 1488, 1182, 1122, 927; ^1H NMR ($CDCl_3$) 1.78 (3H, s), 3.79 (2H, d, J= 6.9 Hz), 3.85 (2H,m), 4.35 (1H, m); 5 to 5.4 (4H, m), 5.75 (1H, m), 5.95 (1H, m), 5.95 (1H, m), 7.3 (5H, m); ^{13}C NMR ($CDCl_3$) 24.4 (CH_3), 31.1 (SCH_2), 33.3 (SCH_2), 80.8 (C-Ph), 119.3 (CH_2), 119.4 (CH_2), 125.7 (CH), 128.3 (CH), 128.7 (CH), 131.4 (CH), 133.4 (CH), 137.1 (Cq), 156.4 (Cq), 168.2 (Cq); MS (EI, m/z): 318 $(M)^+$, 302 $(M- O)^+$, 261 $(302-allyl)^+$; Anal. Calcd for $C_{16}H_{18}N_2OS_2$: C, 60.34; H, 5.69; N, 8.79; S, 20.13 Found: C, 60.42; H, 5.74; N, 8.84; S, 20.21.

2,5-Diallylthio-4,4-diphenyl-(4H)-imidazole-1-oxide ***15b.*** This compound was prepared from **10b** in a manner analogous to that used for the preparation of **15a** and formed pale yellow crystals (53%), m.p. 51 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 1597, 1482, 1216, 1137, 1111, 986, 928; ^1H NMR ($CDCl_3$) 3.8 (2H, dt, J_1= 6.9 Hz, J_2= 1.1 Hz), 4.09 (2H, d, J= 7.1Hz), 4.8 to 5.4 (5H, m), 5.95 (1H, m), 7.3 (10H, m); ^{13}C NMR ($CDCl_3$) 31.9 (SCH_2), 33.4 (SCH_2), 87.9 (C-Ph_2), 119.3 (CH_2), 119.5 (CH_2), 127.8 (CH), 128.3 (CH), 128.6 (CH), 131.5 (CH), 132.4 (CH), 138.7 (Cq), 154.3 (Cq), 168 (Cq); MS (EI, m/z): 380 $(M)^+$; Anal. Calcd for $C_{21}H_{20}N_2OS_2$: C, 66.28; H, 5.30; N, 7.36; S, 16.85 Found: C, 66.36; H, 5.29; N, 7.37; S, 16.78.

Preparation of 4,4-Disubstituted-2-alkylthio-1-hydroxy-4,5-dihydroimidazole-5-thiones (16a-e, 17a-b and 18).

General procedure: Sodium hydrosulfide (405 mg, 7.2 mmoles) was added to a solution of compounds **13a-e**, **14a-b** or **15b** (6 mmoles) in DMF (6ml) cooled to 0°C. After the addition the resulting mixture was allowed to warm to room temperature and the reaction was stirred for a further 1hr. The solution was then diluted with ether and extracted into a dilute aqueous K_2CO_3 solution and water. The extracts were combined and washed with ether, then acidified with 6N HCl and, finally, re-extracted into ether. This ether layer was dried ($MgSO_4$), filtered and evaporated to dryness to give the pure thiohydroxamic acids. Compounds **17a-b** and **18** were not stable in solution and could not be recrystallized. Their ^1H and ^{13}C NMR were obtained immediately after evaporation of the solvent.

1-Hydroxy-2-methylthio-4-methyl-4-phenyl-4,5-dihydroimidazole-5-thione ***16a.*** This compound formed yellow crystals (91%), m.p. 140-142 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3040, 1585, 1574, 1449, 1402, 1201, 1022, 899; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 1.74 (3H, s), 2.61 (3H, s), 7.3 (3H, m), 7.4 (2H, m); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 12.6 (SCH_3), 27.3 (CH_3), 82.2 (C-Ph), 125.6 (CH), 127.3 (CH), 127.7 (CH), 139.7 (Cq), 162.4 (Cq), 206.1 (C=S); MS (EI, m/z): 252 $(M)^+$, 235 $(M\text{- }OH)^+$; Anal. Calcd for $C_{11}H_{12}N_2OS_2$: C, 52.35; H, 4.79; N, 11.10; S, 25.41 Found: C, 52.48; H, 4.84; N, 11.03; S, 25.33.

4,4-Diphenyl-1-hydroxy-2-methylthio-4,5-dihydroimidazole-5-thione ***16b.*** This compound formed yellow crystals (78%), m.p. 147-149 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3040, 1586, 1569, 1458, 1400, 1226, 1173, 1124, 956; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 2.61 (3H, s), 7.3 (6H, m), 7.4 (4H, m), 11.9 (1H, OH, br); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 12.6 (SCH_3), 87.9 (C-Ph), 127.4 (CH), 127.6 (CH), 127.7 (CH), 140.7 (Cq), 162.2 (Cq), 203.4 (C=S); MS (EI, m/z): 314 $(M)^+$, 297 $(M\text{- }OH)^+$; Anal. Calcd for $C_{16}H_{14}N_2OS_2$: C, 61.11; H, 4.49; N, 8.91; S, 20.39 Found: C, 61.18; H, 4.49; N, 8.93; S, 20.39.

4,4-Di-p-anisyl-1-hydroxy-2-methylthio-4,5-dihydroimidazole-5-thione ***16c.*** This compound formed colorless crystals (69%), m.p. 159 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3005, 1604, 1569, 1505, 1456, 1229, 1174, 1031, 830; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 2.62 (3H, s), 3.76 (3H, s), 6.8 (4H, d), 7.34 (4H, d), 11.9 (1H, OH, br); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 12.5 (SCH_3), 54.7 (OCH_3), 87.1 (C-(p-MeO-$C_6H_4)_2$), 112.7 (CH), 128.7 (CH), 132.8 (Cq), 158.4 (Cq), 161.4 (Cq), 204 (C=S); Anal. Calcd for $C_{18}H_{18}N_2O_3S_2$: C, 57.73; H, 4.84; N, 7.48; S, 17.12 Found: C, 57.67; H, 4.88; N, 7.51; S, 17.22.

4,4-Di-p-chlorophenyl-1-hydroxy-2-methylthio-4,5-dihydroimidazole-5-thione ***16d.*** This compound formed yellow crystals (66%), m.p. 160 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3200, 1580, 1564, 1485, 1459, 1393, 1175, 1093, 825; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 2.31 (3H, s), 7.28 (4H, d), 7.42 (4H, d), 12.15 (1H, OH, br); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 12.6 (SCH_3), 86.4 (C-(p-Cl-$C_6H_4)_2$), 127.6 (CH), 129 (CH), 133.1 (Cq), 139 (Cq), 163 (Cq), 202.1 (C=S); Anal. Calcd for $C_{16}H_{12}Cl_2N_2OS_2$: C, 50.13; H, 3.15; N, 7.30; S, 16.73 Found: C, 50.22; H, 3.16; N, 7.28; S, 16.68.

1-Hydroxy-2-methylthio-4-methyl-4-p-nitrophenyl-4,5-dihydroimidazole-5-thione ***16e.*** This compound was obtained as a yellow solid (89%), m.p. 157 °C ; IR (CH_2Cl_2, cm^{-1}) 1603, 1517, 1346, 1201, 851; ^1H NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 1.8 (3H, s), 2.64 (3H, s), 7.73 (2H, d), 8.14 (2H, d), 11.8 (1H, OH, br); ^{13}C NMR ($CDCl_3$-$(CD_3)_2SO$ 1:1) 12.6 (SCH_3), 28.1 (CH_3), 81.6 (C-CH_3), 122.7 (CH), 126.9 (CH), 146.6 (Cq), 146.7

(Cq), 163.6 (Cq), 204.5 (C=S); MS (EI, m/z): 297 $(M)^+$, 280 $(M- OH)^+$, 207 $(M- CH_3SCNOH)^+$; Anal. Calcd for $C_{11}H_{11}N_3O_3S_2$: C, 44.42; H, 3.73; N, 14.13; S, 21.56 Found: C, 44.53; H, 3.73; N, 14.05; S, 21.50.

2-Benzylthio-1-hydroxy-4-methyl-4-phenyl-4,5-dihydroimidazole-5-thione **17a.** This was a yellow oil (70%); IR (CH_2Cl_2, cm^{-1}) 3032, 1571, 1450, 1398, 1197, 1129; ^1H NMR ($CDCl_3$) 1.68 (3H, s), 4.5 (2H, s), 7.2 to 7.4 (10H, m), 8.55 (1H, OH, br); ^{13}C NMR ($CDCl_3$) 27.6 (CH_3), 35 (CH_2), 83 (C-Ph), 126 to 129.2 (CH), 135.1 (Cq), 138.8 (Cq), 160.4 (Cq), 204 (C=S).

2-Benzylthio-4,4-diphenyl-1-hydroxy-4,5-dihydroimidazole-5-thione **17b.** This was a yellow oil (81%); ^1H NMR ($CDCl_3$) 4.51 (2H, s), 7.3 to 7.5 (15H, m), 8.8 (1H, OH, br); ^{13}C NMR ($CDCl_3$) 35 (SCH_2), 88.8 (C-Ph_2), 127.6 to 129.3 (CH), 135.5 (Cq), 140 (Cq), 157.9 (Cq), 198.9 (C=S).

2-Allylthio-4,4-diphenyl-1-hydroxy-4,5-dihydroimidazole-5-thione **18.** This was a yellow oil (85%); ^1H NMR ($CDCl_3$) 3.95 (2H, dd, J_1= 6.9 Hz, J_2= 1.1 Hz), 5.22 (1H, dd, J_1= 10 Hz, J_2= 0.9 Hz), 5.4 (1H, dd, J_1= 17 Hz, J_2= 1.2 Hz), 6 (1H, m), 7.3 (6H, m), 7.45 (4H, m), 9.3 (1H, OH, br); ^{13}C NMR ($CDCl_3$) 33.3 (SCH_2), 88.7 (C-Ph_2), 119.6 (CH_2), 127.9 (CH), 128.1 (CH), 131.6 (Cq), 140.2 (Cq), 158.2 (Cq), 200.4 (C=S).

Preparation of the Selenohydroxamic Acid (21):

4,4-Diphenyl-1-hydroxy-2-methylthio-4,5-dihydroimidazole-5-selenone **21.** Absolute ethanol (10 ml) was added slowly to a mixture of selenium powder (397 mg, 5.03 mmol) and sodium borohydride (250 mg, 6.57 mmol) under argon at 0°C. The reaction mixture was stirred until the solution became colorless. The solution of NaSeH was then added slowly, via a cannula, to a solution of the N-Oxide **13b** (1.5 g, 4.57 mmol) in EtOH (10 ml), at 0°C and under argon. After the addition, the resulting mixture was stirred for a further 1hr at 0°C. The solution was then diluted with dichloromethane and extracted into a dilute aqueous $NaHCO_3$ solution and water. The extracts were combined, washed twice with dichloromethane, then acidified with 6N HCl and, finally re-extracted into dichloromethane. The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness, at room temperature and in the dark, to give the pure selenohydroxamic acid **21** (1.5 g, 91%) as an orange solid, m.p. 127 °C ; IR (CH_2Cl_2, cm^{-1}) 3054, 1586, 1576, 1458, 1212, 1181, 1127; ^1H NMR ($CDCl_3$) 2.71 (3H, s), 7.3 (6H, m), 7.48 (4H, m), 9.2 (1H, OH, br); ^{13}C NMR ($CDCl_3$) 13.6 (SCH_3), 128.1 (CH), 128.2 (CH), 139 (Cq); MS (EI, m/z) 362 $(MH)^+$, 345 $(M- O)^+$, 266 $(345- Se)^+$.

Preparation of 4,4-Disubstituted-1-palmitoyloxy-imidazolidine-2,5-dithiones (11a-e):

General procedure: Palmitoyl chloride (1 mmol) was added at -20°C to a stirred solution of the thiohydroxamic acid **10a-e** (1mmol) and pyridine (1mmol) in dry ether (10 ml). The reaction mixture was stirred in the dark for 30 min at -20°C. Then the solution was quickly washed with water. The ether layer was dried over $MgSO_4$, filtered and evaporated to dryness, at room temperature and in the dark, to give the palmitoyl derivatives (**11a-e**) pure by ^1H and ^{13}C NMR .

4-Methyl-1-palmitoyloxy-4-phenyl-imidazolidine-2,5-dithione **11a.** This compound formed pale yellow crystals (85%), m.p. 55 °C (hexane); IR (CH_2Cl_2, cm^{-1}) 3412, 1812, 1480, 1369, 1309, 1210, 1125; ^1H NMR ($CDCl_3$) 0.88 (3H, t), 1.26 (24H, m), 1.75 (2H, m), 1.98-2 (3H, 2s), 2.62 (2H, t), 7.38 (5H, m), 8.3 (1H, NH, br); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.7 to 31.9 (CH_2 and CH_3CPh), 74.5 (C-Ph), 125.7 (CH), 126 (CH), 129 (CH),

129.1 (CH), 138.4 (Cq), 168 168.1 (C=O), 176.4 176.5 (C=S), 198.2 198.3 (C=S); Anal. Calcd for $C_{26}H_{40}N_2O_2S_2$: C, 65.50; H, 8.45; N, 5.87; S, 13.45 Found: C, 65.33; H, 8.47; N, 5.82; S, 13.86.

4,4-Diphenyl-1-palmitoyloxy-imidazolidine-2,5-dithione ***11b***. This formed yellow crystals (86%), m.p. 93 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3403, 1811, 1475, 1365, 1308, 1166, 1127, 1051; ^1H NMR ($CDCl_3$) 0.87 (3H, t), 1.25 (24H, m), 1.78 (2H, m), 2.65 (2H, m), 7.3 to 7.5 (10H, m), 8,72 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.6 to 31.8 (CH_2), 80.8 (C-Ph$_2$), 127.8 to 129 (CH), 138.2 (Cq), 139.8 (Cq), 167.9 (C=O), 175.7 (C=S), 195.1 (C=S); Anal. Calcd for $C_{31}H_{42}N_2O_2S_2$: C, 69.10; H, 7.85; N, 5.20; S, 11.90 Found: C, 69.20; H, 7.88; N, 5.26; S, 12.01.

4,4-Di-p-anisyl-1-palmitoyloxy-imidazolidine-2,5-dithione ***11c***. This was a yellow oil (92%), IR (film) 3268, 1809, 1603, 1494, 1461, 1253, 1176, 827; ^1H NMR ($CDCl_3$) 0.88 (3H, t), 1.26 (24H, m), 1.78 (2H, m), 2.65 (2H, t), 3.77 (3H, s), 3.79 (3H, s), 6.86 (4H, 2d), 7.23 (2H, d), 7.34 (2H, d), 8.6 (1H, NH, br); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.7 to 31.9 (CH_2), 55.3 (OCH_3), 55.4 (OCH_3), 80.2 (C-(p-MeO-C_6H_4)$_2$), 113.9 (CH), 114 (CH), 128.9 (CH), 129.4 (CH), 130.3 (Cq), 132 (Cq), 159.8 (Cq), 159.9 (Cq), 168 (C=O), 175.5 (C=S), 196.1 (C=S).

4,4-Di-p-chlorophenyl-1-palmitoyloxy-imidazolidine-2,5-dithione ***11d***. This was a yellow solid (95%), IR (CH_2Cl_2, cm^{-1}) 3403, 1813, 1474, 1312, 1094; ^1H NMR ($CDCl_3$) 0.85 (3H, t), 1.3 (24H, m), 1.75 (2H, m), 2.65 (2H, t), 7.3 (8H, m), 8.6 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.7 to 29.9 (CH_2), 79.6 (C-(p-Cl-C_6H_4)$_2$), 129 (CH), 129.2 (CH), 129.3 (CH), 135.5 (Cq), 135.6 (Cq), 136.3 (Cq), 138 (Cq), 167.9 (C=O), 175.8 (C=S), 194.2 (C=S).

4-Methyl-4-p-nitrophenyl-1-palmitoyloxy-imidazolidine-2,5-dithione ***11e***. This was a yellow oil (95%) ; IR (CH_2Cl_2, cm^{-1}) 3336, 1811, 1483, 1345; ^1H NMR ($CDCl_3$) 0.86 (3H, t), 1.23 (24H, m), 1.75 (2H, m), 2.05 (3H, s), 2.62 (2H, t), 7.65 (5H, m), 8.2 (2H, d), 8.7 (1H, NH, br); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.6 to 31.8 (CH_2 and CH_3CPh), 73.7 73.9 (C-CH_3), 124 124.3 (CH), 127 127.3 (CH), 144.8 145.2 (Cq), 148 (Cq), 167.9 168.1 (C=O), 176.5 (C=S), 196.4 (C=S).

Preparation of 4,4-Disubstituted-2-methylthio-1-palmitoyloxy-4,5-dihydroimidazole-5-thiones (19a-e).

General procedure: Palmitoyl chloride (1 mmol) was added at 0°C to a stirred solution of **16a-e** (1 mmol) and pyridine (1 mmol) in dry dichloromethane (10 ml). The reaction was stirred in the dark for 30 min at 0°C. Then the solution was quickly washed with water, dried over $MgSO_4$, filtered and evaporated to dryness, at room temperature in the dark, to give the pure palmitoyl derivatives **19a-e** .

4-Methyl-2-methylthio-1-palmitoyloxy-4-phenyl-4,5-dihydroimidazole-5-thione ***19a***. This compound formed pale yellow crystals (79%), m.p. 49 °C (hexane); IR (CH_2Cl_2, cm^{-1}) 1810, 1577, 1354, 1210, 1053; ^1H NMR ($CDCl_3$) 0.9 (3H, t), 1.3 (24H, m), 1.75 (2H, m), 1.9 (3H, s), 2.6 (2H, t), 2.65 (3H, s), 7.3 (3H, m), 7.5 (2H, m); ^{13}C NMR ($CDCl_3$) 13 (CH_3), 14 (CH_3), 22.6 to 29.8 (CH_2 and CH_3CPh), 83 83.3 (C-Ph), 126 (CH), 127.8 (CH), 128.3 (CH), 139.4 (Cq), 159.4 (Cq), 168.1 (C=O), 207.4 (C=S); MS (EI, m/z): 446 (M- CO_2)$^+$, 235 (M-$OCOC_{15}H_{31}$)$^+$, Anal. Calcd for $C_{27}H_{42}N_2O_2S_2$: C, 66.07; H, 8.62; N, 5.71; S, 13.06 Found: C, 66.20; H, 8.64; N, 5.65; S, 13.01.

4,4-Diphenyl-2-methylthio-1-palmitoyloxy-4,5-dihydroimidazole-5-thione ***19b***. This compound formed yellow crystals (88%), m.p. 54 °C (hexane); IR (CH_2Cl_2, cm^{-1}) 1811, 1586, 1571, 1355, 1126, 1046; ^1H NMR ($CDCl_3$) 0.89 (3H, t), 1.28 (24H, m), 1.78 (2H, m), 2.6 (5H, SCH_3 and $COCH_2$, 1s+1m), 7.3 (8H, m), 7.6 (2H, m); ^{13}C NMR ($CDCl_3$) 13 (CH_3), 14.1 (CH_3), 22.6 to 31.9 (CH_2), 88.8 (C-Ph_2), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.3 (CH), 140 (Cq), 141.5 (Cq), 159.1 (Cq), 168.1 (C=O), 204.4 (C=S); MS (EI, m/z): 508 (M-CO_2)$^+$, 297 (M- $OCOC_{15}H_{31}$)$^+$; Anal. Calcd for $C_{32}H_{44}N_2O_2S_2$: C, 69.52; H, 8.02; N, 5.06; S, 11.60. Found: C, 69.57; H, 8.06; N, 5.09; S, 11.51.

4,4-Di-p-anisyl-2-methylthio-1-palmitoyloxy-4,5-dihydroimidazole-5-thione ***19c***. This was a yellow oil (93%), IR (film) 1809, 1583, 1570, 1346, 1298, 1247, 1172, 826; ^1H NMR ($CDCl_3$) 0.87 (3H, t), 1.25 (24H, m), 1.75 (2H, m), 2.62 (5H, CH_2CO and SCH_3, 1t+1s), 3.78 (6H, s), 6.85 (4H, d), 7.3 (2H, d), 7.5 (2H, d); ^{13}C NMR ($CDCl_3$) 13.1 (CH_3), 14.1 (CH_3), 22.7 to 31.9 (CH_2), 55.2 (OCH_3), 88.2 (C-(p-CH_3O-C_6H_4)$_2$), 113.4 (CH), 129.3 (CH), 132.2 (Cq), 133.9 (Cq), 158.7 (Cq), 159.2(Cq), 168.2 (C=O), 205.3 (C=S); MS (EI, m/z): 568 (M-CO_2)$^+$, 357 (M- $OCOC_{15}H_{31}$)$^+$.

4,4-Di-p-chlorophenyl-2-methylthio-1-palmitoyloxy-4,5-dihydroimidazole-5-thione ***19d***. This was a yellow oil (96%), IR (CH_2Cl_2, cm^{-1}) 1812, 1583, 1567, 1486, 1354, 1250, 1093, 1041, 826; ^1H NMR ($CDCl_3$) 0.89 (3H, t), 1.27 (24H, m), 1.75 (2H, m), 2.66 (5H, CH_2CO and SCH_3, 1t+1s), 7.3 (6H, m), 7.5 (2H, m); ^{13}C NMR ($CDCl_3$) 13.1 (CH_3), 14.1 (CH_3), 22.7 to 29.9 (CH_2), 87.5 (C-(p-Cl-C_6H_4)$_2$), 128.4 (CH), 129.5 (CH), 134.2 (Cq), 134.3 (Cq), 138.2 (Cq), 139.8 (Cq), 160.1 (Cq), 168.1 (C=O), 203.6 (C=S); MS (EI, m/z): 576 (M-CO_2)$^+$, 365 (M- $OCOC_{15}H_{31}$)$^+$.

4-Methyl-2-methylthio-4-p-nitrophenyl-1-palmitoyloxy-4,5-dihydroimidazole-5-thione ***19e***. This was a yellow oil (96%); IR (film) 1810, 1578, 1515, 1345, 1266, 1210, 1051, 850; ^1H NMR ($CDCl_3$) 0.86 (3H, t), 1.24 (24H, m), 1.75 (2H, m), 1.88 (3H, s), 2.59 (2H, t), 2.67 (3H, br), 7.72 (3H, m), 8.16 (2H, d); ^{13}C NMR ($CDCl_3$) 13.1 (CH_3), 14.1 (CH_3), 22.6 to 31.8 (CH_2 and CH_3CPh), 82.2 82.5 (C-Ph), 123.3 (CH), 123.5 (CH), 127.3 (CH), 146.5 146.6 (Cq), 147.4 (Cq), 160.8 (Cq), 168.1 (C=O), 205.7 (C=S); MS (EI, m/z): 491 (M-CO_2)$^+$, 280 (M-$OCOC_{15}H_{31}$)$^+$.

Preparation of the Selenone Derivative (22):

4,4-Diphenyl-2-methylthio-1-palmitoyloxy-4,5-dihydroimidazole-5-selenone ***22***. Palmitoyl chloride (336 µl, 1 eq) was added at -20°C to a stirred solution of **21** (400 mg, 1.108 mmol) and pyridine (90 µl, 1 eq) in dry ether (10 ml). The reaction was stirred in the dark for 30 min at -20°C. Then the solution was quickly washed with water, dried over $MgSO_4$, filtered and evaporated to dryness, at room temperature and in the dark, to give **22** (631 mg, 95%) as an orange oil; IR (CH_2Cl_2, cm^{-1}) 1811, 1588, 1350, 1043; ^1H NMR ($CDCl_3$) 0.89 (3H, t), 1.27 (24H, m), 1.7 (2H, m), 2.66 (5H, $COCH_2$ and SCH_3, m), 7.3 (8H, m), 7.6 (2H, m); ^{13}C NMR ($CDCl_3$) 13.5 (SCH_3), 14.1 (CH_3), 22.6 to 29.9 (CH_2), 92.8 (C-Ph), 127.8 (CH), 127.9 (CH), 128 (CH), 128.4 (CH), 138.6 (Cq), 140.2 (Cq), 159.5 (N=C-S), 167.7 (C=O), 209 (C=Se).

Products of Photolysis (12a-e, 20a-e, 23):

General procedure : To a solution of the palmitoyl derivatives **11a-e** or **19a-e** or **22** (0.7 mmol) in $CDCl_3$ (7 ml), previously degassed, was added propyl acetate (50 µl) as an internal standard. This solution was divided in 10 aliquots (0.7 ml in 10 NMR tubes) which were photolysed at 0°C with visible light (270 watt): two tungsten lamps (150 W and 120 W) were placed at about 10 cm from the aligned NMR tubes kept in an ice bath. The NMR tubes were removed at different times and placed in the dark.The percentage of starting material left at these different times was then calculated by ^1H NMR ($t_{1/2}$ measurement). Then, all the aliquots were photolysed for a further 1hr, combined and the solvent removed under vacuum. The residues were then chromatographed on silica gel (ether - hexane in a gradient) to give the rearranged products **12a-e** or **20a-e** or **23**.

4-Methyl-5-palmitylthio-4-phenyl-2,3-(4H)-dihydroimidazole-2-thione ***12a.*** This formed pale yellow crystals (60%), m.p.101 °C (ether - hexane); IR (CH_2Cl_2, cm^{-1}) 3421, 1487, 1442, 1115; ^1H NMR ($CDCl_3$) 0.89 (3H, t), 1.26 (24H, m), 1.65 (2H, m), 1.91 (3H, s), 3.24 (2H, t), 7.3 (2H, m), 7.4 (3H, m), 9.3 (1H, NH, br); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.6 to 32.1 (CH_2 and $\underline{C}H_3CPh$), 78 ($\underline{C}$-Ph), 125.4 (CH), 129 (CH), 129.2 (CH), 136.9 (Cq), 193.9 (Cq), 201 (C=S); MS (EI, m/z): 432 $(M)^+$, 417 $(M- CH_3)^+$,222 $(MH- C_{15}H_{31})^+$, 190 $(MH- SC_{15}H_{31})^+$.Anal. Calcd for $C_{25}H_{40}N_2S_2$: C, 69.38; H, 9.31 Found: C, 69.34; H, 9.35.

4,4-Diphenyl-5-palmitylthio-2,3-(4H)-dihydroimidazole-2-thione ***12b.*** This compound formed pale yellow crystals (72%), m.p. 97 °C (dichloromethane - hexane); IR (CH_2Cl_2, cm^{-1}) 3415, 1482, 1439, 1121; ^1H NMR ($CDCl_3$) 0.9 (3H, t), 1.3 (24H, m), 1.7 (2H, m), 3.3 (2H, t), 7.33 (10H, m), 9.6 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.6 to 32.8 (CH_2), 85.5 ($\underline{C}$-Ph), 127.5 (CH), 128.9 (CH), 138.1 (Cq), 193.2 (Cq), 197.6 (C=S); MS (EI, m/z): 494 $(M)^+$, 462 $(M- S)^+$, 417 $(M- Ph)^+$, 252 $(MH- SC_{15}H_{31})^+$; Anal. Calcd for $C_{30}H_{42}N_2S_2$: C, 72.82; H, 8.55 Found: C, 72.82; H, 8.59.

4,4-Di-p-anisyl-5-palmitylthio-2,3-(4H) dihydroimidazole-2-thione ***12c.*** This was a yellow oil (68%); IR (CH_2Cl_2, cm^{-1}) 3413, 1605, 1485, 1443, 1176, 1123, 829; ^1H NMR ($CDCl_3$) 0.95 (3H, t), 1.22 (24H, m), 1.68 (2H, m), 3.28 (2H, t), 3.78 (6H, s), 6.85 (4H, d), 7.2 (4H, d), 9.8 (1H, NH, s); ^{13}C NMR ($CDCl_3$) 14 (CH_3), 22.5 to 32.6 (CH_2), 55.2 (OCH_3), 84.7 ($\underline{C}$-(p-MeO-C_6H_4)$_2$), 114.1 (CH), 128.7 (CH) 129.9 (Cq), 159.7 (Cq), 192.7 (Cq) 198.1 (C=S); MS (EI, m/z): 522 $(M- S)^+$, 312 $(MH- SC_{15}H_{31})^+$. Anal. Calcd for $C_{32}H_{46}N_2O_2S_2$: C, 69.26; H, 8.35 Found: C, 69.00; H, 8.34.

4,4-Di-p-chlorophenyl-5-palmitylthio-2,3-(4H)-dihydroimidazole-2-thione ***12d.*** This was a yellow oil (62%); IR (CH_2Cl_2, cm^{-1}) 3409, 1480, 1439, 1121, 1094, 825; ^1H NMR ($CDCl_3$) 0.9 (3H, t), 1.3 (24H, m), 1.7 (2H, m), 3.3 (2H, t), 7.2 (4H, d), 7.35 (4H, d), 10 (1H, NH, br); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.7 to 33.1 (CH_2), 84.5 ($\underline{C}$-(p-Cl-C_6H_4)$_2$), 128.9 (CH), 129.4 (CH), 135.4 (Cq), 136.2 (Cq), 193.1 (Cq), 196.9 (C=S); MS (EI, m/z): 530 $(M- S)^+$, 417 $(M- SC_{15}H_{31})^+$.

4-Methyl-4-p-nitrophenyl-5-palmitylthio-2,3-(4H)-dihydroimidazole-2-thione ***12e.*** This was a yellow oil (55%); IR (CH_2Cl_2, cm^{-1}) 3415, 1523, 1489, 1440, 1346, 1121, 1099, 853; ^1H NMR ($CDCl_3$) 0.84 (3H, t), 1.22 (24H, m), 1.65 (2H, m), 1.94 (3H, s) 3.22 (2H, t), 7.48 (2H, d), 8.2 (2H, d), 9.6 (1H, NH, br); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 22.6 to 32.5 (CH_2 and $\underline{C}H_3CPh$), 77.5 ($\underline{C}$-CH_3), 124.3 (CH), 126.7 (CH), 148 (Cq), 148 (Cq), 194.1 (Cq), 198.7 (C=S); MS (EI, m/z): 267 $(M- C_{15}H_{31})^+$.

4-Methyl-2-methylthio-5-palmitylthio-4-phenyl-(4H)-imidazole **20a**. This formed colorless crystals (97%), m.p. 47 °C ; IR (CH_2Cl_2, cm^{-1}) 1540, 1482, 1193, 1117, 1047; ^1H NMR ($CDCl_3$) 0.9 (3H, t), 1.25 (24H, m), 1.65 (2H, m), 1.73 (3H, s), 2.6 (3H, s), 3.15 (2H, t), 7.29 (5H, m); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 14.2 (CH_3), 22.7 to 32.6 (CH_2 and $\underline{C}H_3CPh$), 87.1 ($\underline{C}$-Ph), 125.6 (CH), 127.9 (CH), 128.6 (CH), 138.5 (Cq), 173.9 (Cq), 203.5 (Cq); MS (EI, m/z): 446 $(M)^+$, 235 $(M- C_{15}H_{31})^+$; Anal. Calcd for $C_{26}H_{42}N_2S_2$: C, 69.89; H, 9.47 Found: C, 69.99; H, 9.43.

4,4-Diphenyl-2-methylthio-5-palmitylthio-(4H)-imidazole **20b**. This compound was obtained as a colorless solid (95%), m.p. 69 °C ; IR (CH_2Cl_2, cm^{-1}) 1536, 1481, 1162, 1097; ^1H NMR ($CDCl_3$) 0.89 (3H, t), 1.28 (24H, m), 1.7 (2H, m), 2.61 (3H, s), 3.21 (2H, t), 7.3 (10H, m); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 14.3 (CH_3), 22.7 to 33.3 (CH_2), 94.7 ($\underline{C}$-Ph), 127.9 (CH), 128.1 (CH), 128.4 (CH), 140 (Cq), 173.6 (Cq), 201.3 (Cq); Anal. Calcd for $C_{31}H_{44}N_2S_2$: C, 73.17; H, 8.71 Found: C, 73.11; H, 8.72.

4,4-Di-p-anisyl-2-methylthio-5-palmitylthio-(4H)-imidazole **20c**. This was a yellow oil (96%); IR (CH_2Cl_2, cm^{-1}) 1605, 1504, 1482, 1460, 1175, 1160, 1095, 828; ^1H NMR ($CDCl_3$) 0.9 (3H, t), 1.3 (24H, m), 1.7 (2H, m), 2.62 (3H, s), 3.2 (2H, t), 3.8 (6H, s), 6.85 (4H, d), 7.23 (4H, d); ^{13}C NMR ($CDCl_3$) 14 (CH_3), 14.2 (CH_3), 22.6 to 33.2 (CH_2), 55.1 (CH_3), 93.8 ($\underline{C}$-(p-MeO-C_6H_4)$_2$), 113.6 (CH), 129 (CH), 132 (Cq), 159.1 (Cq), 173 (Cq) 201.8 (Cq); Acc. Mass: 568.3157 Found: 568.3141.

4,4-Di-p-chlorophenyl-2-methylthio-5-palmitylthio-(4H)-imidazole **20d**. This was a colorless oil (97%); IR (CH_2Cl_2, cm^{-1}) 1535, 1483, 1162, 1110, 1093, 822; ^1H NMR ($CDCl_3$) 0.88 (3H, t), 1.27 (24H, m), 1.7 (2H, m), 2.59 (3H, s), 3.22 (2H, t), 7.24 (8H, 2d); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 14.3 (CH_3), 22.7 to 33.5 (CH_2), 93.5 ($\underline{C}$-(p-Cl-C_6H_4)$_2$), 128.6 (CH), 129.2 (CH), 134.1 (Cq), 138.1 (Cq), 174.4 (Cq) 200.4 (Cq); Acc. Mass: 576.2166 Found: 576.2165.

4-Methyl-2-methylthio-5-palmitylthio-4-p-nitrophenyl-(4H)-imidazole **20e**. This formed colorless crystals (75%), m.p. 76 °C (hexane) ; IR (CH_2Cl_2, cm^{-1}) 1519, 1481, 1346, 1117, 1047; ^1H NMR ($CDCl_3$) 0.88 (3H, t), 1.26 (24H, m), 1.65 (2H, m), 1.77 (3H, s), 2.62 (3H, s), 3.17 (2H, t), 7.44 (2H, d), 8.2 (2H, d); ^{13}C NMR ($CDCl_3$) 14 (CH_3), 14.3 (CH_3), 22.6 to 32.8 (CH_2 and $\underline{C}H_3CPh$), 86.6 ($\underline{C}$-CH_3), 123.7 (CH), 126.8 (CH), 145.9 (Cq), 147.4 (Cq), 175.3 (Cq), 202 (Cq); MS (EI, m/z): 491 $(M)^+$, 280 $(M-C_{15}H_{31})^+$; Anal. Calcd for $C_{26}H_{41}N_3O_2S_2$: C, 63.50; H, 8.40 Found: C, 63.26; H, 8.43.

4,4-Diphenyl-2-methylthio-5-palmitylseleno-(4H)-imidazole **23**. This was obtained as colorless solid (100%), m.p. 64 °C ; IR (CH_2Cl_2, cm^{-1}) 1536, 1481, 1147, 1085, 1065; ^1H NMR ($CDCl_3$) 0.89 (3H, t), 1.26 (24H, m), 1.8 (2H, m), 2.63 (3H, s), 3.27 (2H, t), 7.3 (10H, m); ^{13}C NMR ($CDCl_3$) 14.1 (CH_3), 14.3 (CH_3), 22.6 (CH_2), 28.9 to 29.7 (CH_2), 31.9 (CH_2), 96 ($\underline{C}$-Ph_2), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 139.6 (Cq), 173.9 (N=$\underline{C}$-S), 202.3 (N=$\underline{C}$-Se); Anal. Calcd for $C_{31}H_{44}N_2SSe$: C, 66.99; H, 7.98 Found: C, 66.95; H, 8.01.

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