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# Synthesis and Reactivity of Tetrahydroimidazo [1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thiones

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1,3-Dipolar cycloaddition of imidazoline 3-oxides **1** with methylisothiocyanate proceeds regio- and diastereoselectively to give tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thiones **3** in high yields. The *cis* configuration of the adducts was proved by our double *cis* elimination test as well as by NOESY experiments. Adducts **3a-c** undergo ring opening at reflux in acetonitrile to give imidazoles while **3d-e** undergo retro dipolar cycloaddition to give the starting nitrones **1d-e**. The imidazooxadiazol-2-thiones **3a-e** were treated with concentrated HCl in ethanol at 50 °C to give the corresponding 4*H*-[1,2,4]oxadiazole-5-thione only in cases in which the substituent at C-6 is an aryl.

**Key Words:** Imidazoline 3-oxides, 1,3-Dipolar cycloaddition, Tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thiones, 4*H*-[1,2,4]oxadiazole-5-thione.

## Introduction

A number of works either on cycloadditions or incorporating cycloadditions have appeared in recent years.<sup>1</sup> 1,3-Dipolar cycloadditions of nitrones, with a variety of dipolarophiles, are important in the synthesis of 5-membered heterocyclic compounds.<sup>1-4</sup> Aryl and alkylisothiocyanates also act as dipolarophiles with respect to C=N bonds but in some cases cycloaddition may occur at C=S in the reaction with different nitrones.<sup>4</sup> While nitrones undergo cycloaddition to the C=N double bond of phenylisothiocyanates to give the corresponding oxadiazole-5-thiones, in reactions with substituted phenylisothiocyanates and benzoylisothiocyanate addition to the C=S double bond predominates.<sup>5-6</sup> The cycloaddition reactions with alkylisothiocyanates are analogous to the reaction with arylisothiocyanates.<sup>6</sup> The reaction of acyclic nitrones with isothiocyanates was shown to give mainly oxadiazolidin-5-thiones.<sup>7</sup> We have shown the 1,3-dipolar cycloaddition reactions of cyclic nitrones **1** with dipolarophiles as arylisocyanates,<sup>8-9</sup> styrene,<sup>10</sup> DMAD,<sup>11-12</sup> and  $\beta$ -pinene<sup>13</sup> to proceed regio- and, in the case of chiral nitrones, diastereoselectively. When heated, the adducts from isocyanates and styrene undergo retro 1,3-dipolar cycloaddition, while the adducts from DMAD and  $\beta$ -pinene give the corresponding imidazoles. The most interesting feature of the adducts from isocyanate,<sup>14</sup> DMAD<sup>11-12</sup> and chiral nitrones **1** was their different behavior in the presence of secondary

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and tertiary amines. A quite reliable chemical way, double *cis* elimination, was developed for determination of the relative configuration of the carbons 3a and 6 in the tetrahydroimidazooxadiazol-2-ones, and tetrahydroimidazoisoxazolines.<sup>11–12,14</sup>

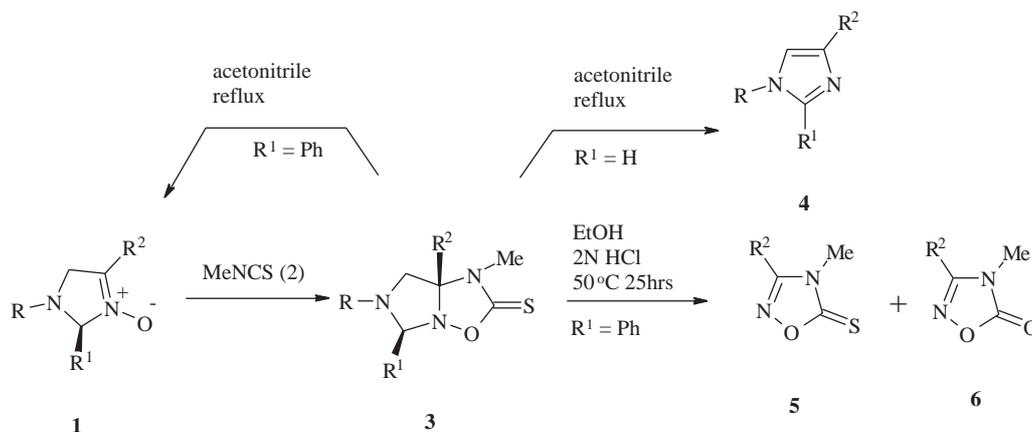
Recently, we reported our preliminary results<sup>15</sup> on the 1,3-dipolar cycloaddition of nitrones **1** and methylisothiocyanate and the ring opening reactions of the adducts formed. Here we report in detail the reaction of cyclic nitrones **1** with a 4-fold excess of methylisothiocyanate in acetonitrile, **method A**, and with twenty fold excess of the dipolarophile without solvent, **method B**, to give a new class of tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thiones **3**. Methylisothiocyanate was shown to react regio- and diastereoselectively with nitrones **1d-e**. The configuration of their adducts **3d-e** was confirmed as *cis* by our double *cis* elimination test<sup>11–12,14</sup> as well as by a NOESY experiment. The behaviour of adducts **3** in a warm solution and the condensed phase, and the reactions of **3** with secondary and tertiary amines are reported. An interesting rearrangement of C-6 substituted adducts **3** in the presence of HCl to give 4*H*-[1,2,4]oxadiazole-5-thione and its possible mechanism are also discussed.

## Results and Discussion

Cyclic nitrones **1** were refluxed in acetonitrile in the presence of phenylisothiocyanate for 48 h but no conversion to the corresponding imidazooxadiazol-2-thiones was observed; the nitrones were recovered unchanged. This was in contrast with the reaction of the same nitrones with arylisocyanates, in which the reaction proceeds in high yields to give the corresponding imidazooxadiazol-2-ones.<sup>14</sup> However, nitrones **1** gave the corresponding oxadiazol-2-thiones, **method A**, in low yields when refluxed in acetonitrile for 4 h in the presence of a 4-fold excess of methylisothiocyanate. The yields of **3** and unreacted **1** are given in the Table. Prolonging the reaction time did not improve the yields, instead lower or no yields were obtained after 48 and 64 h respectively. In the latter cases the main product formed was the corresponding imidazole. High yields were achieved by performing the reaction using the dipolarophile as a solvent, **method B** (see Table 1). When 12 mmolar acetonitrile solutions of **3a-c** were refluxed for 17 h, a quantitative conversion to imidazole **4a-c** was observed. The analogous experiment revealed that 36 h reflux of 12 mmolar acetonitrile solution of **3d-e** led mainly to imidazole **4d-e** while the more diluted solution (2 mM) led to the corresponding nitrone **1d-e** after 72 h in 80% yield. However, the 2 mmolar solution of **3c** did not give the corresponding nitrone **1c**; it gave the corresponding **4c**. The ring opening of **3a-e** when concentrated solutions are used to give imidazoles and the retro dipolar cycloaddition of C-6 phenyl substituted adducts to give nitrones **1** when diluted solutions are used is unique behaviour among the tetrahydroimidazo adducts reported in our earlier studies.<sup>8–13</sup>

The structures of compounds **3** were established on the basis of their IR, <sup>1</sup>H, and <sup>13</sup>C NMR spectra and elemental analysis. The absence of absorption in the 1510-1650 cm<sup>-1</sup> region of the IR spectra of compounds **3** was indicative of the regioisomer arising from the addition to the C=N double bond. Alternative addition to the C=S bond should give an exocyclic imine having a C=N stretching vibration in the mentioned region.<sup>6</sup> Characteristic patterns of adducts **3a-c** are the 2 proton AB systems at 3.73 ( $J_{AB} = 10.8$  Hz) and 4.72 ppm ( $J_{AB} = 10.8$  Hz) assigned to C-4 and C-6 methylenes. The AB system for C-4 protons of **3d-e** appears at nearly 4.20 ppm and the singlet for the C-6 proton has  $\delta$  5.92 and 6.02 for **3d** and **3e** respectively. These chemical shifts are in good agreement with those for the same protons in the adducts obtained from the same imidazoline 3-oxides and phenylisocyanate where the *cis* relation of the phenyls at C-3a and C-6 was

deduced from NOE and double *cis* elimination amine test experiments. The thiocarbonyl carbon's shifts in the  $^{13}\text{C}$  NMR spectra of compounds **3** are at  $\delta$  183 ppm approximately.



Scheme 1

Table 1. Tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thiones **3**, imidazoles **4** and oxadiazolethione **5**.

	Yields of <b>3</b>		R	R <sup>1</sup>	R <sup>2</sup>	mp of <b>3</b> (°C)	Yields of <b>6</b>	
	Meth. A	Meth. B					<b>4</b> <sup>b</sup>	<b>5</b>
<b>a</b>	15 (80) <sup>a</sup>	65	4-MeC <sub>6</sub> H <sub>4</sub>	H	Ph	116.6	98	0
<b>b</b>	22 (70)	70	4-MeOC <sub>6</sub> H <sub>4</sub>	H	4-MeOC <sub>6</sub> H <sub>4</sub>	155-155.6	94	0
<b>c</b>	15 (80)	70	4-MeOC <sub>6</sub> H <sub>4</sub>	H	Ph	98	95	0
<b>d</b>	30 (65)	90	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	Ph	149.8	95	56
<b>e</b>	20 (70)	95	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	Ph	146.3-147	97	60

<sup>a</sup>The yields of the recovered **1**. <sup>b</sup>Thermal ring opening was performed at temperatures of 118, 165, 90, 150, 143 °C for **3a**, **3b**, **3c**, **3d**, and **3e** respectively under vacuum ( $1.3 \times 10^{-3}$  mm Hg) for 10 min.

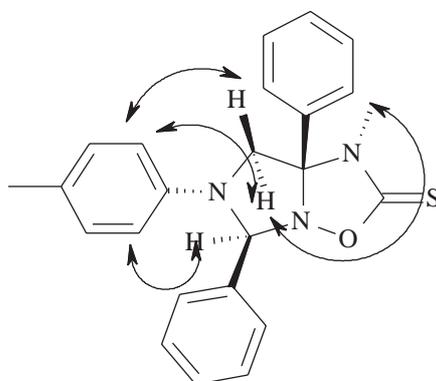
We assume that due to steric hindrance the dipolarophile should attack nitrones **1d-e** from the opposite side of the phenyl at C-2. This results in *cis* 3a,6-diphenylimidazooxadiazol-2-thiones **3d-e**, which is the case in all of the tetrahydroimidazo adducts reported.<sup>8-13</sup>

The reaction of **3d** with aniline (1:2 molar ratio) in ethanol at reflux for 24 h gave the corresponding nitron **1** and N-methyl-N-phenylurea. This is in agreement with the reaction of arylisocyanate adducts with aniline where the products were also nitron **1** and the corresponding N,N-diarylurea.

Thermal treatment of adducts **3** in the condensed phase under vacuum at the temperatures given in the Table led to the formation of corresponding imidazoles in high yields. The same reaction with the adducts of nitrones **1** with arylisocyanates led to the formation of corresponding nitrones.<sup>8,9</sup> The reflux of compounds **3a-e** at the concentration mentioned above in acetonitrile for 48 h gave the same imidazoles as in the condensed phase reaction, while the reflux of the diluted solution of **3d-e** led to the formation of nitrones **1d-e**. It is clear from these experiments that the reaction between methylisothiocyanate and nitrones **1** is a reversible process and in more concentrated solutions it seems that the isothiocyanate formed catalyzes the elimination of methylthiocarbamic acid to give the corresponding imidazole, while in low concentrations the retro reaction is favored, probably due to the consumption of the isothiocyanate in a hydrolysis reaction (water from the moisture of the acetonitrile).

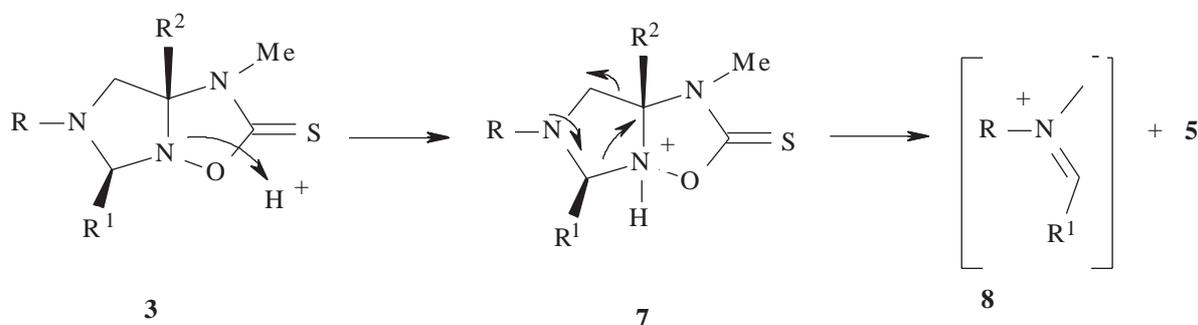
Adducts **3a-c** are converted to the corresponding **4** within 30-40 min in the presence of diethyl- or triethylamine in refluxing acetonitrile. Adducts **3d-e** were refluxed for 4 h with an excess of diethylamine expecting a double *cis* elimination as in the cases of DMAD and isocyanate<sup>14</sup> adducts. This was the case; imidazole **4** was the only product formed. However, the same adducts remained unchanged, as did the *cis* DMAD<sup>11-12</sup> adducts. The *cis* structure was confirmed by X-ray analysis, under the same conditions as when triethylamine was used. *cis* Arylisocyanate adducts also gave no elimination but underwent retro cycloaddition when treated with triethylamine for a long time.<sup>14</sup>

Some selected NOESY correlations for **3e** are given in the figure below. Methyls protons are in clear relation with the part of the AB system at C-4. This proton, in turn, gives a cross peak with the protons of the *p*-tolyl ring. The proton at C-6 also gives a cross peak with the protons of the aryl at N-5. All these give a reliable base for the assignment of the *cis* configuration for compounds **3d-e**.



**Figure.** Selected NOESY correlations for **3e**.

Compound **3a** with  $R^1 = H$  slowly gives the corresponding imidazole when heated gently on a water bath in ethanol in the presence of 37% HCl while **3c** remains unchanged.<sup>16</sup> However, at the same reaction conditions adducts **3d-e** having  $R^1 = Ar$  were identified to give 4*H*-[1,2,4]oxadiazole-5-thione **5** and 4*H*-[1,2,4]oxadiazole-5-one **6**. The probable mechanism of the reaction is outlined in Scheme 2. Protonation of adduct **3** at the bridgehead nitrogen leads to the formation of an ammonium species **7**, which undergoes retro 1,3-dipolar cycloaddition to give the corresponding azomethine ylide **8** and oxadiazol-5-thione **5**. To the best of our knowledge this is the first example of acid induced rearrangement of tetrahydroimidazooxadiazol-5-thiones.



**Scheme 2**

Azomethine ylide formation was deduced from its hydrolysis products, namely the aldehyde and the corresponding amine. Thus the method described serves as an alternative cycloaddition way of obtaining oxadiazol-5-thiones by the reaction of N-substituted amide oximes with ethyl chloroformate and thiophosgene.<sup>17–18</sup>

Compound **6** was isolated in 36 and 35% yields from the reaction mixtures of **3d** and **3e**, respectively. Compound **6** should arise from the rearrangement of the hydrolyzed products of **3d** and **3e** since attempts to hydrolyze isolated compound **5** in ethanol in the presence of 37% HCl for 40 h did not give any **6**. Compound **6** was treated with P<sub>2</sub>S<sub>5</sub> in xylene to give quantitative amounts of compound **5**.

## Experimental

Melting points were recorded on an Electrothermal Digital melting point apparatus. IR spectra were recorded on a Mattson 1000 FTIR. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Dpx 400 MHz spectrometer. All spectra were taken in deuteriochloroform with a little DMSO-d<sub>6</sub>. Freshly prepared imidazoline 3-oxides<sup>19–21</sup> were used after recrystallization from either ethanol or acetone.

**Tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thiones 3a-e; General procedure. Method A-** To a suspension of imidazoline 3-oxide **1** (2 mmol) in acetonitrile (10 mL) was added methylisothiocyanate (8 mmol) and the mixture was refluxed for 4 h. The solvent and the excess of isothiocyanate were removed under vacuum. The residue was subjected to column chromatography using silica gel as an adsorbent and ethyl acetate petroleum ether (1:3) as an eluent. Further purification was performed by recrystallization from ethanol.

**Method B-** A mixture of imidazoline 3-oxide **1** (2 mmol) and methylisothiocyanate (20 mmol) was heated for 2 h at 80 °C. Excess isothiocyanate was removed under vacuum and the residue was dissolved in ethanol under heating and was left to crystallize at room temperature. The formed white crystals were separated by filtration and dried under vacuum.

**3-Methyl-3a-phenyl-5-*p*-tolyl-tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thione (3a)** IR (KBr) No absorption corresponding to  $\nu_{C=N}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub> and DMSO-d<sub>6</sub>)  $\delta$  ppm 2.27 (3H, s), 3.0 (3H, s), 3.46 (1H, d, *J* = 10.7), 4.2 (1H, d, *J* = 10.78), 4.36 (1H, d, *J* = 10.7), 5.07 (1H, d, *J* = 10.78), 6.68 (2H, d, *J* = 7.7), 7.05 (2H, d, *J* = 7.6), 7.43-7.54 (5H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub> and DMSO-d<sub>6</sub>)  $\delta$  ppm 20.11; 31.04; 53.94; 75.46; 93.46; 115.02; 126.44; 128.64; 129.16; 129.46; 129.49; 135.51; 142.68; 182.42.

Calcd. for C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>OS C, 66.43; H, 5.88; N, 12.91; S, 9.85. Found C, 66.84; H, 6.31; N, 12.67; S, 9.47.

**3-Methyl-3a,5-di(4-methoxyphenyl)-tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thione (3b)** IR (KBr) No absorption corresponding to  $\nu_{C=N}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub> and DMSO-d<sub>6</sub>)  $\delta$  ppm 2.96 (3H, s), 3.33 (1H, d, *J* = 10.7), 3.73 (3H, s), 3.82 (3H, s), 4.08 (1H, d, *J* = 10.9), 4.43 (1H, d, *J* = 10.7), 5.06 (1H, d, *J* = 10.9), 6.79 (4H, s), 6.94 (2H, d, *J* = 7.9), 7.46 (2H, d, *J* = 7.9). <sup>13</sup>C NMR (CDCl<sub>3</sub> and DMSO-d<sub>6</sub>)  $\delta$  ppm 30.96; 54.70; 75.98; 54.87; 54.92; 93.61; 113.93; 114.33; 116.58; 127.56; 128.04; 139.12; 153.52; 160.16; 182.05.

Calcd. for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>S C, 61.44; H, 5.70; N, 11.31; S, 8.63. Found C, 60.95; H, 5.27; N, 11.16; S, 8.34.

**3-Methyl-3a-phenyl-5-(4-methoxyphenyl)-tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2(1*H*)-thione (3c)** No absorption corresponding to  $\nu_{C=N}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm 2.93 (3H, s), 3.40 (1H, d, *J*

= 10.55), 3.70 (3H, s), 4.11 (1H, d,  $J = 11.05$ ), 4.14 (1H, d,  $J = 10.83$ ), 4.99 (1H, d,  $J = 10.85$ ), 6.67 (2H, d,  $J = 8.81$ ), 6.80 (2H, d,  $J = 8.78$ ), 7.39-7.44 (5H, m).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 31.94; 55.19; 77.00; 56.04; 94.54; 115.35; 117.23; 127.21; 129.59; 130.50; 136.11; 139.53; 154.59; 183.57.

Calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$  C, 63.32; H, 5.61; N, 12.31; S, 9.39. Found C, 62.87; H, 5.90; N, 12.20; S, 9.00.

**3-Methyl-3a,6-diphenyl-5-(4-methoxyphenyl)-tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2 (1*H*)-thione (3d)** No absorption corresponding to  $\nu_{\text{C}=\text{N}}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 3.0 (3H, s), 3.7 (3H, s), 4.18 (1H, d,  $J = 11$ ), 4.23 (1H, d,  $J = 11$ ), 5.92 (1H, s), 6.63 (2H, d,  $J = 8.46$ ), 6.73 (2H, d,  $J = 8.46$ ), 7.2-7.24 (3H, m), 7.31-7.42 (7H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 31.94; 55.72; 87.23; 55.87; 92.61; 115.24; 116.88; 126.94; 127.86; 128.86; 128.99; 129.38; 130.02; 136.19; 136.97; 139.55; 154.11; 183.63.

Calcd. for  $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$  C, 69.04; H, 5.55; N, 10.06; S, 7.68. Found C, 69.70; H, 5.42; N, 9.27; S, 6.83.

**3-Methyl-3a,6-diphenyl-5-(4-methylphenyl)-tetrahydroimidazo[1,5-*b*][1,2,4]oxadiazol-2 (1*H*)-thione (3e)** No absorption corresponding to  $\nu_{\text{C}=\text{N}}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 2.24 (3H, s), 3.0 (3H, s), 4.21 (1H, d,  $J = 11$ ), 4.29 (1H, d,  $J = 11$ ), 6.02 (1H, s), 6.56 (2H, d,  $J = 7.9$ ), 6.98 (2H, d,  $J = 7.8$ ), 7.19-7.24 (3H, m), 7.3-7.4 (7H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 20.86; 31.94; 54.68; 87.18; 92.82; 114.77; 126.97; 127.70; 128.90; 128.94; 129.05; 129.35; 130.04; 130.36; 135.96; 136.99; 143.25; 183.58.

Calcd. for  $\text{C}_{24}\text{H}_{23}\text{N}_3\text{OS}$  C, 71.79; H, 5.77; N, 10.46; S, 7.99. Found C, 70.97; H, 5.41; N, 10.29; S, 7.61.

**Thermal ring opening of compounds 3a-e.** Imidazooxadiazol-2-thiones **3** (0.1 mmol) were heated in a vacuum oven under vacuum ( $1.3 \times 10^{-3}$  mm Hg) at 90-165 °C for 10 min. The imidazole formed was extracted with hexane (3 x 2 mL). The combined extracts were concentrated and left to crystallize.

**Reaction of 3a-e with secondary amines.** To a solution of **3** (0.3 mmol) in acetonitrile (13 mL) was added diethylamine (8 mL) and the mixture was refluxed at stirring for 3 h. The solvent was evaporated and the residue recrystallized to give the corresponding imidazole **4**.

**Reaction with tertiary amines.** To a solution of **3** (0.3 mmol) in acetonitrile (13 mL) was added triethylamine (8 mL) and the mixture refluxed at stirring for 3h. The solvent was evaporated and the residue recrystallized to give the corresponding imidazole **4** in the cases of **3a-c** and the unreacted adducts **3** in the cases of **3d-e**.

**The reaction of 3d-e with HCl.** To a suspension of **3** (0.15 mmol) in ethanol (20 mL) was added HCl (0.13 mL, 37%) and the mixture heated at 50 °C on a water bath for 25 h. The solvent was removed and the residue extracted with dichloromethane (3 x 15 mL). The combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent removed under vacuum. The products isolated by recrystallization or column chromatography were the corresponding *4-Methyl-3-phenyl-4H-[1,2,4]oxadiazole-5-thione*, mp 117-118 °C ; lit<sup>18</sup> mp 119-120 and *4-Methyl-3-phenyl-4H-[1,2,4]oxadiazole-5-one*, lit<sup>22</sup> mp 119-120 °C.

**Reaction with  $\text{HClO}_4$ .** To a solution of **3a** (0.100 g, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) was added 70%  $\text{HClO}_4$  (4mL) and the mixture stirred at room temperature for 40 min. The mixture was basified with ammonia and the organic phase was separated, dried and filtered and the organic solvent evaporated. The residue was recrystallized from petroleum ether to give the corresponding imidazole **4a**. Yield 92% .

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