Syntheses of Substituted-oxazolo-1,3,4-thiadiazoles, 1,3,4-Oxadiazoles, and 1,2,4-Triazoles

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Starting from readily available methyl 5-methyloxazole-4-carboxylate (**1**) and 4-methyl-5-oxazolylcarboxylic acid hydrazide (**11**) the title compounds were prepared. The reaction of compound **1** with hydrazine hydrate afforded the corresponding hydrazide **2**. The reaction of compound **2** with formic acid yielded 1-formyl-2-(5-methyloxazole-4-carboxyl)hydrazine (**3**). Refluxing of the latter with phosphorus pentasulfide in xylene gave compound **5** in 62% yield. The reaction of compound **3** with phosphorus pentoxide afforded compound **4**. Starting from hydrazide **11**, compounds **13** and **14** were prepared similarly. Reaction of compound **2** with substituted isothiocyanate yielded compound **9** which was cyclized in basic medium to 4-alkyl-5-(5-methyl-4-oxazolyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**10**). The isomer **19** was prepared similarly. Methylation and subsequent oxidation of compound **19** gave compound **21**. Reaction of the acid **7** with thiosemicarbazide in the presence of phosphorus oxychloride gave 2-amino-5-(5-methyl-4-oxazolyl)1,3,4-thiadiazole (**8**). 2-Amino-5-(4-methyl-5-oxazolyl)-1,3,4-thiadiazole (**17**) was prepared from acyl chloride **15** by the usual method.

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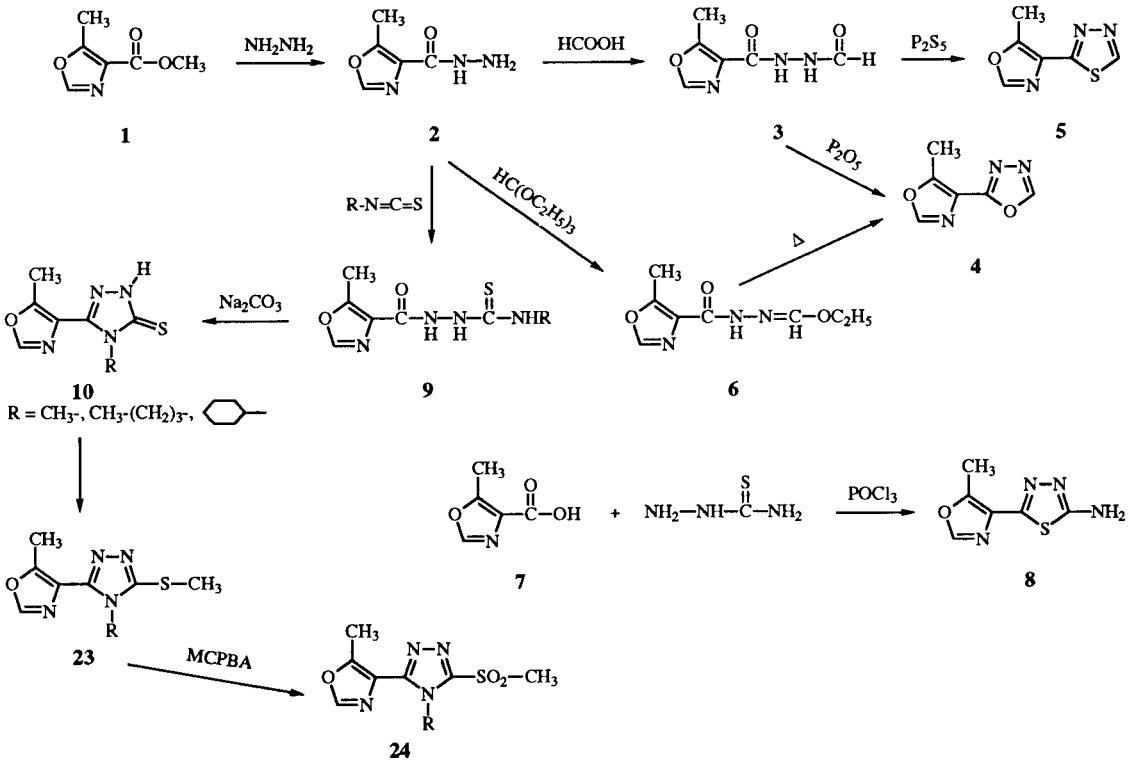
In view of the potential biological activity of members of the 1,2,4-triazole, 1,3,4-thiadiazole, and 1,3,4-oxadiazole ring systems [1,3], it was of interest to us to prepare the title compounds as possible drugs effective against tropical diseases [4].

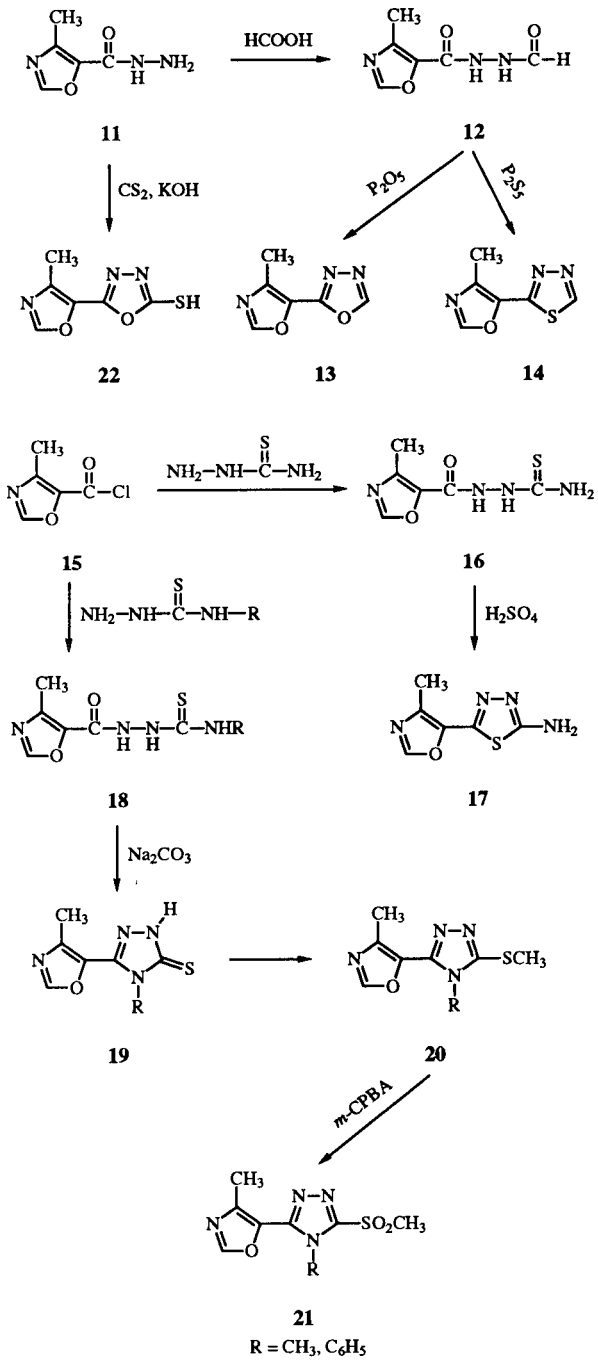
The syntheses of the title compounds was accomplished as shown in Schemes 1 and 2.

The reaction of methyl 5-methyloxazole-4-carboxylate (**1**) [5] with hydrazine hydrate gave 5-methyloxazole-4-carboxylic acid hydrazide (**2**) in high yield. Refluxing compound **2** with formic acid for 30 minutes afforded 1-formyl-2-(5-methyloxazole-4-carboxyl)hydrazine (**3**). Refluxing 0.01 mole of compound **3** with 0.006 mole phosphorus pentasulfide yielded 2-(5-methyl-4-oxazolyl)-

Scheme 1



Scheme 2



1,3,4-thiadiazole (**5**).

The usual reaction for the formation of 1,3,4-oxadiazole, namely the reaction of compound **3** with ethyl orthoformate, did not give the desired compound 2-(5-methyl-4-oxazolyl)-1,3,4-oxadiazole (**4**). In the latter reaction ethoxyformaldehyde 5-methyloxazole-4-carboxyhydrazone (**6**) was formed. Heating compound **6** gave 2-(5-methyl-4-oxazolyl)-1,3,4-oxadiazole (**4**) in 35% yield. Compound **4** could also be obtained in 50% yield by refluxing compound **3** with phosphorus pentoxide in xylene.

Starting from 4-methyloxazole-5-carboxylic acid hydrazide (**11**) [6], compounds **13** and **14** were prepared similarly. Reaction of compound **11** with carbon disulfide in basic medium gave 2-(4-methyl-5-oxazolyl)-1,3,4-oxadiazole-5-thiol (**22**).

Reaction of 5-methyloxazole-4-carboxylic acid (**7**) with phosphorus oxychloride and thiosemicarbazide under the condition reported previously [7] afforded 2-amino-5-(5-methyl-4-oxazolyl)-1,3,4-thiadiazole (**8**).

Reaction of 4-methyloxazole-5-carboxylic acid with phosphorus oxychloride and thiosemicarbazide did not give 2-amino-5-(4-methyl-5-oxazolyl)-1,3,4-thiadiazole (**17**). However the latter could be prepared from the reaction of 4-methyl-5-oxazolecarbonyl choride (**15**) [8] with thiosemicarbazide in pyridine and the subsequent reaction of the intermediate **16** with sulfuric acid.

Reaction of compound **2** with alkyl or phenyl isothiocyanate in ethanol at room temperature [9] gave 1-(5-methyloxazole-4-carboxyl)-4-alkyl-(or phenyl-)thiosemicarbazide (**9**). Refluxing compound **9** with aqueous sodium carbonate solution afforded 4-alkyl-(or phenyl-)-5-(5-methyl-4-oxazolyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**10**).

Reaction of compound **15** with 4-methyl-(or phenyl-)-thiosemicarbazide in pyridine yielded compound **18**. The latter was converted to compound **19** in basic medium.

Methylation of compound **19** with methyl iodide afforded 3-(4-methyl-5-oxazolyl)-4-methyl-(or phenyl-)-5-methylthio-4*H*-1,2,4-triazole (**20**). Oxidation of compound **20** with *m*-chloroperbenzoic acid gave 3-(4-methyl-5-oxazolyl)-4-methyl-(or phenyl-)-5-methylsulfonyl-4*H*-1,2,4-triazole (**21**).

Methylation of compound **10** with methyl iodide and subsequent oxidation of the intermediate **23** afforded 3-(5-methyl-4-oxazolyl)-4-phenyl-5-methylsulfonyl-4*H*-1,2,4-triazole (**24**).

EXPERIMENTAL

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. The uv spectra were recorded using a Perkin-Elmer Model 550 SE spectrometer. The ir spectra were obtained using a Perkin-Elmer Model 267 spectrograph (potassium bromide disks). The ^{1}H nmr spectra were recorded on a Bruker FT-80 spectrometer and chemical shifts (δ) are in ppm relative to internal tetramethylsilane. The mass spectra were run on a Varian Model MAT-MS-311 spectrometer at 70 ev.

5-Methyloxazole-4-carboxylic Acid Hydrazide (**2**).

To a solution of compound **1** (1.41 g, 0.01 mole) in methanol (15 ml) hydrazine hydrate (2.5 g, 0.05 mole) was added. After 5 minutes the precipitate was filtered and crystallized from ethanol to give 1.20 g (85%) of **2**, mp 141-143°; ir (potassium bromide):

ν 3340, 3120 (NH_2 and NH), 1710 cm^{-1} (C=O); ms: m/z (%) 141 (M^+, 85), 110 (100), 68 (28).

Anal. Calcd. for $C_5H_7N_3O_2$: C, 42.55; H, 4.96; N, 29.79. Found: C, 42.38; H, 5.08; N, 29.61.

1-Formyl-2-(5-methyloxazole-4-carboxyl)hydrazine (**3**).

A solution of compound **2** (1.41 g, 0.01 mole) in formic acid (20 ml) was refluxed for 30 minutes. The solvent was evaporated and the residue was crystallized from methanol to give 1.44 g (85%) of compound **3**, mp 165-167°; ir (potassium bromide): ν 3320, 3260 (NH), 3020 (aromatic), 1690, 1650 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): 8.25 (s, 1H, H-CO), 7.05 (s, 1H, H_2 of oxazole), 2.66 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_6H_7N_3O_3$: C, 42.60; H, 4.14; N, 24.85. Found: C, 42.74; H, 4.02; N, 24.97.

2-(5-Methyl-4-oxazolyl)-1,3,4-thiadiazole (**5**).

To a solution of compound **3** (1.69 g, 0.01 mole) in xylene (200 ml) phosphorus pentasulfide (1.4 g, 0.006 mole) was added. The mixture was refluxed for 45 minutes. The solvent was evaporated and the residue was crystallized from methanol to give 1.03 g (62%) of compound **5**, mp 93-94°; uv (methanol): λ_{max} 261 nm (log ε = 3.01); ^1H nmr (deuteriochloroform): 9.02 (s, 1H, H_5 of thiadiazole), 7.78 (s, 1H, H_2 of oxazole) and 2.75 ppm (s, 3H, CH_3); ms: m/z (%) 167 (M^+, 100), 152 (78), 112 (15), 85 (10).

Anal. Calcd. for $C_6H_5N_3OS$: C, 43.11; H, 2.99; N, 25.15. Found: C, 43.25; H, 3.05; N, 25.02.

Ethoxyformaldehyde 5-Methyloxazole-4-carboxyhydrazone (**6**).

A mixture of compound **2** (282 mg, 2 mmoles) and ethyl orthoformate (2.5 ml) was heated to the boiling point. After the compound was completely dissolved it was cooled. The precipitate was filtered and crystallized from chloroform to give 319 mg (81%) of compound **6**, mp 94-95°; ir (potassium bromide): ν 3360 (NH), 3150 (oxazole), 1660 (C=O), 1640 cm^{-1} (C=N); ^1H nmr (deuteriochloroform): 7.69 (s, 1H, H_2 of oxazole), 6.69 (s, 1H, HC=), 4.29 (q, 2H, CH_2), 2.69 (s, 3H, CH_3), 1.42 ppm (t, 3H, CH_3).

Anal. Calcd. for $C_8H_{11}N_3O_3$: C, 48.73; H, 5.58; N, 21.32. Found: C, 48.87; H, 5.63; N, 21.49.

2-(5-Methyl-4-oxazolyl)-1,3,4-oxadiazole (**4**).

Method A.

Compound **6** (197 mg, 1 mmole) was heated at 96-100° for 25 minutes. The residue was purified by preparative tlc on silica gel using chloroform ethyl acetate (90:10) as the eluent to give 53 mg (35%) of compound **4**, mp 88-89°; ^1H nmr (deuteriochloroform): 8.50 (s, 1H, H_5 of oxadiazole), 7.90 (s, 1H, H_2 of oxazole) and 2.66 ppm (s, 3H, CH_3); ms: m/z (%) 151 (M^+, 100), 136 (97), 123 (22), 110 (73), 96 (30), 81 (21), 68 (46), 53 (45), 51 (10).

Anal. Calcd. for $C_6H_5N_3O_2$: C, 47.68; H, 3.31; N, 27.81. Found: C, 47.59; H, 3.45; N, 27.68.

Method B.

To a solution of compound **3** (1.69 g, 0.01 mole) in xylene (150 ml) phosphorus pentoxide (1.42 g, 0.01 mole) was added. The mixture was refluxed for 1 hour. The solvent was evaporated. To the residue water (5 ml) was added and extracted with chloroform. The solvent was evaporated and the residue was crystallized from methanol to give 0.75 g (50%) of **4**, mp 88-89°.

1-Formyl-2-(4-methyloxazole-5-carboxyl)hydrazine (**12**).

This compound was prepared similarly to compound **3** in 50% yield, mp 136-140°; ir (potassium bromide): ν 3310, 3205 (NH), 3080 (aromatic), 1710 and 1665 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): 8.27 (s, 1H, HCO), 8.0 (s, 1H, H_2 of oxazole), 2.39 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_6H_7N_3O_3$: C, 42.60; H, 4.14; N, 24.85. Found: C, 42.46; H, 4.02; N, 24.96.

2-(4-Methyl-5-oxazolyl)-1,3,4-oxadiazole (**13**).

This compound was prepared similarly to **4** (method B) in 40% yield, mp 84-86° (petroleum ether); uv (methanol): λ_{max} 253 nm (log ε = 4.30); ^1H nmr (deuteriochloroform): 8.51 (s, 1H, H_5 of oxadiazole), 8.0 (s, 1H, H_2 of oxazole), 2.56 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_6H_5N_3O_2$: C, 47.68; H, 3.31; N, 27.81. Found: C, 47.82; H, 3.45; N, 27.94.

2-(4-Methyl-5-oxazolyl)-1,3,4-thiadiazole (**14**).

This compound was prepared similarly to **5** in 60% yield; mp 107-109° (petroleum ether); uv (methanol): λ_{max} 277 nm (log ε = 4.22); ^1H nmr (deuteriochloroform): 9.16 (s, 1H, H_5 of thiadiazole), 7.95 (s, 1H, H_2 of oxazole), 2.60 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_6H_5N_3OS$: C, 43.11; H, 2.99; N, 25.15. Found: C, 43.26; H, 3.06; N, 25.30.

2-(4-Methyl-5-oxazolyl)-1,3,4-oxadiazole-5-thiol (**22**).

To a stirring solution of sodium hydroxide (0.4 g, 0.01 mole) in water (50 ml) and ethanol (50 ml) compound **11** (1.41 g, 0.01 mole) and then carbon disulfide (0.83 g, 0.01 mole) were added. The mixture was refluxed for 3 hours. The solvent was evaporated under reduced pressure. The residue was dissolved in water and filtered. The filtrate was acidified and filtered. The precipitate was crystallized from ethanol to give 0.86 g (47%) of **22**, mp 218-220°; ^1H nmr (deuteriochloroform): 8.18 (s, 1H, H_2 of oxazole), 2.47 ppm (s, 3H, CH_3); ms: m/z (%) 183 (M^+, 100), 123 (95), 110 (24), 82 (98), 54 (85), 42 (93).

Anal. Calcd. for $C_6H_5N_3O_2S$: C, 39.34; H, 2.73; N, 22.95. Found: C, 39.18; H, 2.85; N, 22.83.

2-Amino-5-(5-methyl-4-oxazolyl)-1,3,4-thiadiazole (**8**).

A mixture of acid **7** (12.7 g, 0.1 mole), thiosemicarbazide (9.1 g, 0.1 mole) and phosphorus oxychloride (35 ml) was refluxed gently for half an hour. After cooling, water (100 ml) was added. The mixture was refluxed for 4 hours and filtered. The solution was neutralized with potassium hydroxide. The precipitate was filtered and crystallized from ethanol-water to give 9.1 g (50%) of **8**, mp 272-273°; uv (methanol): λ_{max} 266 nm (log ε = 3.04); ms: m/z (%) 182 (M^+, 83), 167 (63), 152 (70), 112 (18), 70 (10), 56 (10).

Anal. Calcd. for $C_6H_6N_4OS$: C, 39.56; H, 3.30; N, 30.77. Found: C, 39.73; H, 3.15; N, 30.59.

1-(4-Methyloxazole-5-carboxyl)thiosemicarbazide (**16**).

To a stirring solution of thiosemicarbazide (0.91 g, 0.01 mole) in dry pyridine (15 ml) at -5° a solution of compound **15** (1.455 g, 0.01 mole) in dry benzene (15 ml) was added. The stirring was continued for half an hour at -5° and then overnight at room temperature. The solvent was evaporated. To the residue water (30 ml) was added. The precipitate was filtered and crystallized from ethanol to give 1 g (50%) of **16**, mp 235-236°; ir (potassium bromide): ν 3305, 3120 (NH_2 and NH), 1688 cm^{-1} (C=O); ms: m/z (%) 200 (M^+, 20) 183 (13), 167 (67), 166 (23), 154

(51), 138 (100), 110 (66), 82 (41), 57 (51), 42 (44).

Anal. Calcd. for $C_6H_8N_4O_2S$: C, 36.00; H, 4.00; N, 28.00. Found: C, 35.87; H, 3.91; N, 27.88.

1-(4-Methyloxazole-5-carboxyl)-4-methylthiosemicarbazide (**18**, R = CH_3).

This compound was prepared similarly to **16** in 51% yield, mp 221-222° (ethanol).

1-(4-Methyloxazole-5-carboxyl)-4-phenylthiosemicarbazide (**18**, R = C_6H_5).

This compound was prepared similarly to **16** in 55% yield, mp 178-179° (ethanol).

5-Amino-2-(4-Methyl-5-oxazolyl)-1,3,4-thiadiazole (**17**).

To a mixture of concentrated sulfuric acid (20 ml) and water (2 ml) at 120° compound **16** (2 g, 0.01 mole) was added. The mixture was heated at this temperature for half an hour. After cooling it was added to ice-water. The mixture was made alkaline with ammonia. The precipitate was filtered and crystallized from ethanol to give 0.91 g (50%) of **17**, mp 175-176°.

Anal. Calcd. for $C_6H_6N_4OS$: C, 39.56; H, 3.30; N, 30.77. Found: C, 39.38; H, 3.46; N, 30.62.

1-(5-Methyloxazole-4-carboxyl)-4-methylthiosemicarbazide (**9**, R = CH_3).

To a solution of compound **2** (141 mg, 1 mmole) in ethanol (2 ml) methyl isothiocyanate (73 mg, 1 mmole) and sodium hydroxide (40 mg, 1 mmole, as a 2 *N* solution) was added. The mixture was stirred for 24 hours and filtered. The filtrate was acidified with hydrochloric acid. The precipitate was filtered and crystallized from ethanol-water to give 154 mg (72%) of **9** (R = CH_3), mp 153-155°; ir (potassium bromide): ν 3360 (NH), 3250 (NH), 1678 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): 7.82 (s, 1H, H_2 of oxazole), 3.52 (s, 3H, CH_3), 2.63 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_7H_{10}N_4O_2S$: C, 39.25; H, 4.67; N, 26.17. Found: C, 39.14; H, 4.51; N, 26.32.

4-*n*-Butyl-1-(5-methyloxazole-4-carboxyl)thiosemicarbazide (**9**, R = *n*-Butyl).

This compound was prepared similarly to **9** (R = CH_3) in 75% yield, mp 144-145° (ethanol-water).

Anal. Calcd. for $C_{10}H_{16}N_4O_2S$: C, 46.87; H, 6.25; N, 21.87. Found: C, 46.72; H, 6.37; N, 21.98.

4-Cyclohexyl-1-(5-methyloxazole-4-carboxyl)thiosemicarbazide (**9**, R = Cyclohexyl).

This compound was prepared similarly to **9** (R = CH_3) in 72% yield, mp 101-102° (ethanol-water).

Anal. Calcd. for $C_{12}H_{18}N_4O_2S$: C, 51.06; H, 6.38; N, 19.86. Found: C, 51.18; H, 6.24; N, 19.93.

1-(5-Methyloxazole-4-carboxyl)-4-phenylthiosemicarbazide (**9**, R = C_6H_5).

This compound was prepared similarly to **9** (R = CH_3) in 85% yield, mp 131-133° (ethanol-water).

Anal. Calcd. for $C_{12}H_{12}N_4O_2S$: C, 52.17; H, 4.35; N, 20.29. Found: C, 52.07; H, 4.15; N, 20.18.

5-(5-Methyl-4-oxazolyl)-4-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**10**, R = CH_3).

A stirring mixture of compound **9** (R = CH_3, 214 mg, 1 mmole) and 5% aqueous sodium carbonate solution (10 ml) was refluxed for 4 hours. After cooling, the solution was acidified with hydrochloric acid and the precipitate was filtered. The precipitate was crystallized from ethanol to give 157 mg (80%) of **10** (R = CH_3); mp 149-150°; uv (methanol): λ_{max} 255 nm (log ε = 3.72); ^1H nmr (deuteriochloroform): 7.86 (s, 1H, H_2 of oxazole), 3.88 (s, 3H, CH_3N), 2.60 ppm (s, 3H, CH_3); ms: m/z (%) 196 (M^+, 56), 182 (100), 154 (10), 127 (15), 124 (23), 109 (56), 97 (15), 81 (15), 67 (25), 55 (43), 53 (17).

Anal. Calcd. for $C_7H_8N_4OS$: C, 42.86; H, 4.08; N, 28.57. Found: C, 42.77; H, 3.94; N, 28.48.

4-*n*-Butyl-5-(5-methyl-4-oxazolyl)-2,4-dihydro-3*H*-1,2,4-triazole-5-thione (**10**, R = *n*-butyl).

This compound was prepared similarly to **10** (R = CH_3) in 85% yield, mp 154-156° (ethanol).

Anal. Calcd. for $C_{10}H_{14}N_4OS$: C, 50.42; H, 5.88; N, 23.53. Found: C, 50.53; H, 5.69; N, 23.67.

4-Cyclohexyl-5-(5-methyl-4-oxazolyl)-2,4-dihydro-3*H*-triazole-5-thione (**10**, R = cyclohexyl).

This compound was prepared similarly to **10** (R = CH_3) in 83% yield, mp 173-174° (ethanol).

Anal. Calcd. for $C_{12}H_{16}N_4OS$: C, 54.55; H, 6.06; N, 21.21. Found: C, 54.68; H, 5.93; N, 21.38.

5-(5-Methyl-4-oxazolyl)-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**10**, R = C_6H_5).

This compound was prepared similarly to **10** (R = CH_3) in 89% yield, mp 258-260°(ethyl acetate); uv (ethanol): λ_{max} 264 nm (log ε = 4.11); ^1H nmr (deuteriochloroform): 7.58 (s, 1H, oxazole), 7.50 (m, 3H, phenyl), 7.34 (m, 2H, phenyl), 2.51 ppm (s, 3H, CH_3); ms: m/z (%) 258 (M^+, 22), 255 (64), 224 (12), 192 (42), 162 (10), 128 (53), 96 (45), 77 (10), 64 (100).

Anal. Calcd. for $C_{12}H_{10}N_4OS$: C, 55.81; H, 3.88; N, 21.71. Found: C, 55.69; H, 3.99; N, 21.64.

5-(4-Methyl-5-oxazolyl)-4-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**19**, R = CH_3).

This compound was prepared similarly to **10** (R = CH_3) in 71% yield, mp 211-212° (ethanol).

Anal. Calcd. for $C_7H_8N_4OS$: C, 42.86; H, 4.08; N, 28.57. Found: C, 42.73; H, 3.96; N, 28.39.

5-(4-Methyl-5-oxazolyl)-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**19**, R = C_6H_5).

This compound was prepared similarly to **10** (R = CH_3) in 65% yield, mp 208-209° (ethanol).

Anal. Calcd. for $C_{12}H_{10}N_4OS$: C, 55.81; H, 3.88, N, 21.70. Found: C, 55.90; H, 3.72; N, 21.56.

3-(4-Methyl-5-oxazolyl)-4-methyl-5-methylthio-4*H*-1,2,4-triazole (**20**, R = CH_3).

To a stirring solution of compound **19** (196 mg, 1 mmole) in sodium hydroxide (2 mmoles) in ethanol (0.5 ml) was added. The mixture was stirred overnight. It was diluted with water (5 ml). The precipitate was filtered and crystallized from ethyl acetate to give 189 mg (90%) of **20** (R = CH_3), mp 128-129°; nmr (deuteriochloroform): 7.93 (s, 1H, oxazole), 3.70 (s, 3H, NCH_3), 2.78 (s, 3H, CH_3), 2.52 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_8H_{10}N_4OS$: C, 45.71; H, 4.76; N, 26.62. Found: C, 45.82; H, 4.63; N, 26.89.

3-(4-Methyl-5-oxazolyl)-4-phenyl-5-methylthio-4*H*-1,2,4-tria-

zole (**20**, R = C_6H_5).

This compound was prepared similarly to **20** (R = CH_3) in 89% yield, mp 152-153° (ethyl acetate).

Anal. Calcd. for $C_{13}H_{12}N_4OS$: C, 57.35; H, 4.41; N, 20.59. Found: C, 57.22; H, 4.61; N, 20.75.

3-(4-Methyl-5-oxazolyl)-4-methyl-5-methylsulfonyl-4*H*-1,2,4-triazole (**21**, R = CH_3).

To a stirring solution of compound **20** (R = CH_3, 210 mg, 1 mmole) in dichloromethane (10 ml) at 0° *m*-chloroperbenzoic acid (517.5 mg, 3 mmoles) was added. The mixture was stirred at room temperature overnight. The mixture was washed with sodium bicarbonate solution (3 x 5 ml). It was dried (sodium sulfate), filtered and evaporated. The residue was crystallized from ethyl acetate to give 170 mg (70%) of **21** (R = CH_3), mp 157-158°; uv (ethanol): λ_{max} 254 nm (log ε = 4.29); nmr (deuteriochloroform): 8.01 (s, 1H, H_2 of oxazole), 4.12 (s, 3H, CH_3N), 3.59 (s, 3H, CH_3SO_2), 2.57 ppm (s, 3H, CH_3); ms: m/z (%), 242 (M^+, 100), 214 (97), 186 (98), 161 (43), 135 (60), 109 (82), 82 (87), 79 (57), 54 (79), 42 (82).

Anal. Calcd. for $C_8H_{10}N_4O_3S$: C, 39.67; H, 4.13; N, 23.14. Found: C, 39.78; H, 4.25; N, 23.02.

3-(4-Methyl-5-oxazolyl)-4-phenyl-5-methylsufonyl-4*H*-1,2,4-triazole (**21**, R = C_6H_5).

This compound was prepared similarly to **21** (R = CH_3) in 85% yield, mp 124-125° (ethyl acetate).

Anal. Calcd. for $C_{13}H_{12}N_4O_3S$: C, 51.32; H, 3.95; N, 18.42. Found: C, 51.19; H, 4.06; N, 18.31.

3-(5-Methyl-4-oxazolyl)-4-phenyl-5-methylthio-4*H*-1,2,4-triazole (**23**, R = C_6H_5).

This compound was prepared similarly to **20** (R = CH_3) in 95% yield, mp 108-110° (ethyl acetate); uv (ethanol): λ_{max} 253 nm (log ε = 3.97); nmr (deuteriochloroform): 7.71 (s, 1H, oxazole), 7.60 (m, 3H, phenyl), 7.34 (m, 2H, phenyl), 2.81 (s, 3H, CH_3), 2.55 ppm (s, 3H, CH_3); ms: m/z (%) 272 (M^+, 100), 157 (10), 185 (12), 118 (10), 77 (36), 43 (20).

Anal. Calcd. for $C_{13}H_{12}N_4OS$: C, 57.35; H, 4.41; N, 20.59. Found: C, 57.42; H, 4.36; N, 20.68.

3-(5-Methyl-4-oxazolyl)-4-phenyl-5-methylsulfonyl-4*H*-1,2,4-triazole (**24**).

This compound was prepared similarly to **21** (R = CH_3) in 70% yield, mp 169-170° (ethyl acetate); uv (ethanol): λ_{max} 241 nm (log ε = 3.86); nmr (deuteriochloroform): 7.56 (s, 1H, H_2 of oxazole), 7.47 (m, 5H, C_6H_5), 3.49 (s, 3H, CH_3SO_2), 2.68 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{12}N_4O_3S$: C, 51.32; H, 3.95; N, 18.42. Found: C, 51.51; H, 3.78; N, 18.59.

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