

**1,3-DIPOLAR CYCLOADDITION OF NITRONES AND NITRILE
OXIDES TO 5,5-DIMETHYL-3-METHYLENEPYRROLIDINE-2-
THIONE**

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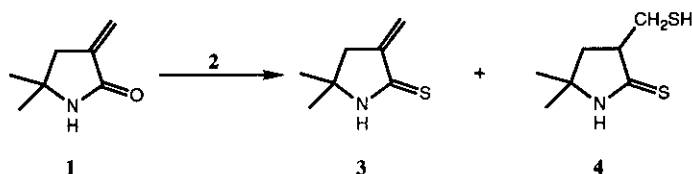
(Dedicated to Prof. Dr. Rolf Huisgen on the occasion of his 75th birthday)

Abstract - A simple synthesis of title compound (**3**) and a number of different cycloadditions are described. *C*-Aroyl- and *C,N*-diphenyl-nitrones react regio- and stereoselectively to the C=C exocyclic double bond of **3**, to give only spirocycloadduct (**10**). On the other hand, *C*-phenyl-*N*-methylnitronone gives a mixture of diastereomeric spirocycloadducts (**10**) and (**11**). Nitrile oxides undergo 1,3-dipolar cycloaddition both to the exocyclic C=C and C=S double bonds with subsequent cycloreversion and formation of spiro-lactams (**6**). The appropriate spiro-thiolactams (**8**) were synthesized by treatment of **6** with Lawesson's reagent.

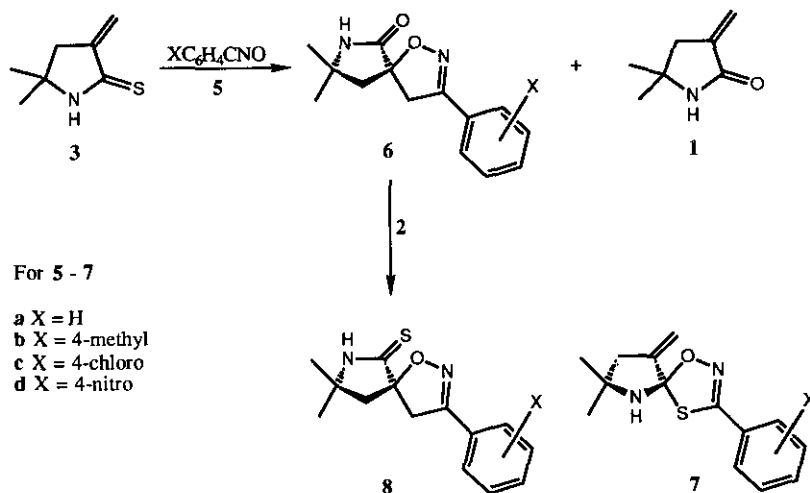
The concept of 1,3-dipolar cycloadditions¹ developed by Huisgen more than 30 years ago has proved to be a very useful method for the synthesis of five membered heterocycles.² In addition to

C=C double bonds, a small number of C=S double bonds have been used as dipolarophiles.^{3,4} The recent observation of the strong herbicidal activity of spirocyclic lactams, coupled with the absence of toxicity to microorganisms⁵ and also that some spiroisoxazolines occur naturally (Araplysillins are inhibitors of ATPase⁶) stimulated our interest in the synthesis of other spirocyclic derivatives. In a continuation of our efforts⁷⁻¹⁰ to utilize heterocyclic compounds as dipolarophiles in 1,3-dipolar cycloaddition reactions, we have recently demonstrated that nitrones⁷ and nitrile oxides⁸ react regio- and stereoselectively with 5,5-dimethyl-3-methylene-2-pyrrolidinone (**1**). In this paper, we report on the cycloaddition of nitrones and nitrile oxides with 5,5-dimethyl-3-methylenepyrrolidine-2-thione (**3**), a dipolarophile possessing both a C=C as well as a C=S double bond.

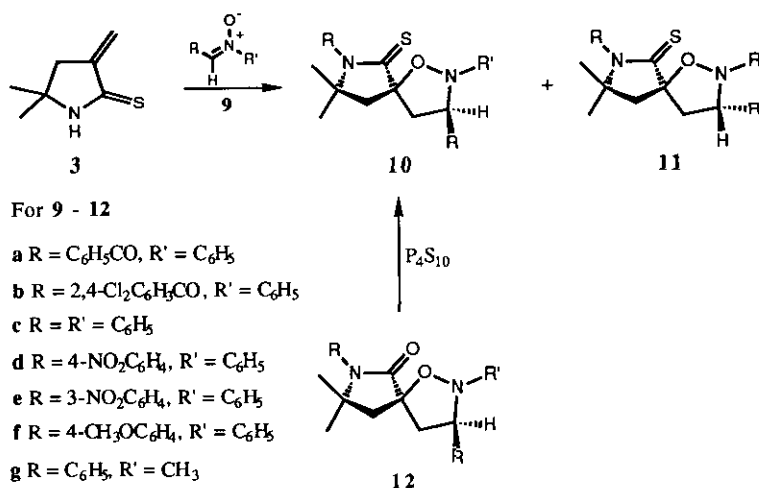
The sulfurization of **1** with P₄S₁₀ proved to be unsatisfactory as a hardly separable mixture of many products was obtained. If, however, **1** was treated in dry tetrahydrofuran at room temperature with 5 equivalents of Lawesson's reagent (**2**), then practically only 5,5-dimethyl-3-methylenepyrrolidine-2-thione (**3**, 85% yield) was produced accompanied with a small amount (5%) of thione (**4**).



The cycloaddition of thione (**3**) with aryl nitrile oxides (**5**) yields the spiro-compounds (**6**) and pyrrolidinone (**1**). It was, however, not possible in this case to isolate the expected spirocyclic (1:1)-adduct to the C=S double bond, namely **7**, which spontaneously eliminated phenylisothiocyanate⁴ to form pyrrolidinone (**1**). The formation of spiro-adduct (**6**), which was already described by us,⁸ can be explained by the subsequent nitrile oxide cycloaddition to **1**. The formation of the (1:1)-adduct (**8**) via cycloaddition to the C=C double bond of **3**, can also be assumed. Its exocyclic C=S double bond then reacts very quickly with a second 1,3-dipole to give a (1:2)-adduct which in turn eliminates phenylisothiocyanate to give **6**. Therefore, the spiro-derivatives (**8**) were obtained independently by the cycloaddition of **1** with nitrile oxides (**5**) followed by sulfurization of so prepared **6** with Lawesson's reagent.



On the other hand, cycloadditions of *C*-(X-benzoyl)- (9a,b) and *C*-(X-phenyl)-*N*-phenylnitrones (9c-g) - where X is H (a), 2,4-diCl (b), H (c), 4-NO₂ (d), 3-NO₂ (e), 4-CH₃O (f) - and 3 proceeded only to the C=C double bond and afforded exclusively the spiro-isoxazolidines (10). The corresponding diastereomer (11) as well as regioisomeric diastereomers have not been detected in the crude reaction mixture by nmr spectroscopy.



The observed stereoselectivity is in contrast to the cycloadditions of *C,N*-diarylnitrones with pyrrolidinone (1), where also the second diastereoisomer was formed as a minor product⁷ (less than 20%). The diastereoselectivity is controlled by steric effects, which is supported by the fact, that

the cycloaddition of *C*-phenyl-*N*-methylnitrone (**9g**) with **3** furnished both diastereoisomers (**10g**) and (**11g**) in a ratio of 51:49 in favour of **10g**. The stereochemical assignment in compounds (**10**) and (**11**) was based on nuclear Overhauser effect difference spectroscopy as well as by the sulfurization of the known spiro-derivatives (**12**) with P_4S_{10} . Interestingly, the cycloadducts (**12**) failed to react with Lawesson's reagent, probably by steric reasons.

EXPERIMENTAL

Melting points were determined on a Kofler hot plate apparatus and are uncorrected. 1H Nmr spectra were recorded on a Varian VXR 300 and Tesla BS 487 C (80 MHz), respectively, and ^{13}C nmr spectra on Varian VXR 300 spectrometers ($CDCl_3$, TMS as internal standard, δ -values in ppm, J in Hz).

5,5-Dimethyl-3-methylenepyrrolidine-2-thione (**3**)

5,5-Dimethyl-3-methylene-2-pyrrolidinone (**1**)¹¹ (0.125 g, 1 mmol) and Lawesson's reagent (**2**) (2.022 g, 5 mmol) in dry tetrahydrofuran (20 ml), were stirred at room temperature for 24 h (tlc). Concentration under reduced pressure and chromatography using chloroform-ethyl acetate gave **3**. Yield 0.120 g (85%); mp 87-88 °C. Anal. Calcd for $C_7H_{11}NS$: C, 59.03; H, 7.86; N, 9.92; S, 22.70. Found: C, 59.06; H, 7.87; N, 9.92; S, 23.00. 1H Nmr: 1.35 (s, 6H, 2 CH_3), 2.75 (d, $J = 2.4$, 2H, H_{2-4}), 5.43 (d, $J = 2.4$, 1H, H_{vinyl}), 6.31 (d, $J = 2.4$, 1H, H_{vinyl}), 9.79 (br s, 1H, NH); ^{13}C nmr: 20.5 (q, 2 CH_3), 42.6 (t, C-4), 61.6 (s, C-5), 119.1, 146.4 (2 C_{vinyl}), 194.0 (s, C=S).

In addition to **3**, 3-mercaptomethyl-5,5-dimethylpyrrolidine-2-thione (**4**) was isolated. Yield 0.009 g (5%); mp 107-108 °C. Anal. Calcd for $C_7H_{13}NS_2$: C, 47.96; H, 7.47; N, 7.99; S, 36.58. Found: C, 47.85; H, 7.37; N, 7.78; S, 36.55. 1H Nmr: 1.35, 1.42 (2 s, 6H, 2 CH_3), 1.66 (br s, 1H, SH), 2.04 (dd, $J = 12.6$ and 9.9, 1H, H_A-4), 2.22 (dd, $J = 12.6$ and 8.4, 1H, H_B-4), 3.00 (m, 2H, CH_2), 3.23 (m, 1H, H-3), 8.84 (br s, 1H, NH); ^{13}C nmr: 27.4 (t, CH_2SH), 28.1, 28.6 (2 q, 2 CH_3), 40.7 (t, C-4), 53.5 (d, C-3), 62.6 (s, C-5), 202.9 (s, C=S).

Nitrile oxide cycloadditions to **3**

Triethylamine (1.512 g, 13 mmol) in ether (30 ml) was added to a stirred solution of arylhydroximoyl chloride (10 mmol) and the dipolarophile (**3**) (1.412 g, 10 mmol) in ether at 0-5 °C within 1 h. The reaction mixture was stirred overnight at room temperature, the solvent was evaporated under diminished pressure, the residue dried, separated by chromatography on a silica gel column, and

purified by crystallization. In addition to pyrrolidinone (1), the previously described⁸ 8,8-dimethyl-3-(X-phenyl)-1-oxa-2,7-diazaspiro[4.4]non-2-en-6-ones (6) - where X is H (6a, 56%), 4-CH₃ (6b, 45%), 4-Cl (6c, 67%) and 4-NO₂ (6d, 71%) - were isolated.

8,8-Dimethyl-3-phenyl-1-oxa-2,7-diazaspiro[4.4]non-2-ene-6-thione (8a)

8,8-Dimethyl-3-phenyl-1-oxa-2,7-diazaspiro[4.4]non-2-en-6-one (6a) (0.244 g, 1 mmol) and 2 (2.022 g, 5 mmol) in dry tetrahydrofuran (20 ml), were stirred at room temperature for 24 h (tlc). Concentration under reduced pressure and chromatography using chloroform-ethyl acetate gave 8a. Yield 0.104 g (40%); mp 254-255 °C. Anal. Calcd for C₁₄H₁₆N₂OS: C, 64.60; H, 6.19; N, 10.76; S, 12.29. Found: C, 64.56; H, 6.23; N, 10.68; S, 12.61. ¹H Nmr: 1.42, 1.54 (2 s, 6H, 2 CH₃), 2.16 (d, J = 13.8, 1H, H_B-9), 2.65 (d, J = 13.8, 1H, H_A-9), 3.26 (d, J = 17.1, 1H, H_A-4), 4.36 (d, J = 17.1, 1H, H_B-4), 7.41 - 7.72 (m, 5H, H_{arom}); ¹³C nmr: 28.8 (q, 2 CH₃), 45.4 (t, C-9), 49.7 (t, C-4), 62.0 (s, C-8), 94.7 (s, C-5), 127.0, 128.7, 129.0, 130.3 (C_{arom}), 155.1 (s, C-3), 200.9 (s, C=S).

From 8,8-dimethyl-3-(4-methylphenyl)-1-oxa-2,7-diazaspiro[4.4]non-2-en-6-one (6b) and 2, 3-(4-methylphenyl)-8,8-dimethyl-1-oxa-2,7-diazaspiro[4.4]non-2-ene-6-thione (8b) was prepared. Yield 30%; mp 267-268 °C. Anal. Calcd for C₁₅H₁₈N₂OS: C, 65.67; H, 6.61; N, 10.21; S, 11.66. Found: C, 65.63; H, 6.56; N, 10.14; S, 11.29. ¹H Nmr: 1.41, 1.53 (2 s, 6H, 2 CH₃), 2.13 (d, J = 14.1, 1H, H_B-9), 2.38 (s, 3H, CH₃), 2.63 (d, J = 14.1, 1H, H_A-9), 3.23 (d, J = 16.8, 1H, H_A-4), 4.32 (d, J = 16.8, 1H, H_B-4), 7.22 - 7.58 (m, 4H, H_{arom}); ¹³C nmr: 21.5 (q, CH₃), 28.8 (q, 2 CH₃), 45.6 (t, C-9), 49.7 (t, C-4), 61.9 (s, C-8), 94.5 (s, C-5), 126.1, 126.8, 126.9, 129.4, 140.5 (C_{arom}), 156.0 (s, C-3), 201.0 (s, C=S).

From 3-(4-chlorophenyl)-8,8-dimethyl-1-oxa-2,7-diazaspiro[4.4]non-2-en-6-one (6c) and 2, 3-(4-chlorophenyl)-8,8-dimethyl-1-oxa-2,7-diazaspiro[4.4]non-2-ene-6-thione (8c) was prepared. Yield 60%; mp 252-253 °C. Anal. Calcd for C₁₄H₁₅N₂OCIS: C, 57.05; H, 5.13; N, 9.50; S, 10.86. Found: C, 56.98; H, 5.18; N, 9.61; S, 10.54. ¹H Nmr: 1.42, 1.54 (2 s, 6H, 2 CH₃), 2.16 (d, J = 13.8, 1H, H_B-9), 2.65 (d, J = 13.8, 1H, H_A-9), 3.23 (d, J = 17.1, 1H, H_A-4), 4.32 (d, J = 17.1, 1H, H_B-4), 7.38 - 7.65 (m, 4H, H_{arom}), 8.39 (br s, 1H, NH); ¹³C nmr: 28.8 (q, 2 CH₃), 45.2, 49.6 (2 t, C-4, C-9), 62.0 (s, C-8), 94.9 (s, C-5), 128.2, 129.0, 136.3 (C_{arom}), 155.2 (s, C-3), 200.6 (s, C=S).

From 8,8-dimethyl-3-(4-nitrophenyl)-1-oxa-2,7-diazaspiro[4.4]non-2-en-6-one (6d) and 2, 8,8-dimethyl-3-(4-nitrophenyl)-1-oxa-2,7-diazaspiro[4.4]non-2-ene-6-thione (8d) was prepared. Yield 62%; mp 250-251 °C. Anal. Calcd for C₁₄H₁₅N₃O₃S: C, 55.08; H, 4.95; N, 13.76; S, 10.48. Found:

C, 54.99; H, 4.87; N, 13.72; S, 10.53. ^1H Nmr: 1.48, 1.52 (2 s, 6H, 2 CH_3), 2.18 (d, $J = 12.0$, 1H, $\text{H}_{\text{B-9}}$), 2.64 (d, $J = 12.0$, 1H, $\text{H}_{\text{A-9}}$), 3.23 (d, $J = 17.1$, 1H, $\text{H}_{\text{A-4}}$), 4.33 (d, $J = 17.1$, 1H, $\text{H}_{\text{B-4}}$), 5.15 (s, 1H, NH), 7.83 - 8.26 (m, 4H, H_{arom}); ^{13}C nmr: 28.83, 28.84 (2 q, 2 CH_3), 45.0, 49.5 (2 t, C-4, C-9), 63.8 (C-8), 96.0 (s, C-5), 127.6, 127.7, 136.5, 147.1 (C_{arom}), 154.9 (s, C-3), 201.3 (s, C=S).

3-Benzoyl-8,8-dimethyl-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (10a)

C-Benzoyl-*N*-phenylnitrone (**9a**) (2.252 g, 10 mmol) and pyrrolidine-2-thione (**3**) (1.412 g, 10 mmol) in benzene (50 ml) was warmed to 40-50 °C within 10 min and then stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure, and the residue purified on silica gel (hexane-ethyl acetate). Yield 2.201 g (60%); mp 169-170 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$: C, 68.83; H, 6.05; N, 7.64; S, 8.73. Found: C, 68.77; H, 6.30; N, 7.68; S, 8.77. ^1H Nmr: 1.34, 1.51 (2 s, 6H, 2 CH_3), 2.14 (d, $J = 13.8$, 1H, $\text{H}_{\text{B-9}}$), 2.62 (dd, $J = 12.6$ and 7.2, 1H, $\text{H}_{\text{A-4}}$), 2.66 (d, $J = 13.8$, 1H, $\text{H}_{\text{A-9}}$), 3.48 (dd, $J = 12.6$ and 8.4, 1H, $\text{H}_{\text{B-4}}$), 5.63 (dd, $J = 8.4$ and 7.2, 1H, H-3), 6.96 - 8.08 (m, 10H, H_{arom}), 8.71 (br s, 1H, NH); ^{13}C nmr: 28.6, 28.8 (2 q, 2 CH_3), 44.3 (t, C-9), 48.8 (t, C-4), 62.2 (s, C-8), 70.2 (d, C-3), 91.6 (s, C-5), 116.5, 122.9, 128.6, 128.9, 133.9, 135.1, 149.9 (C_{arom}), 196.1 (s, C=O), 200.9 (s, C=S).

From C-(2,4-dichlorobenzoyl)-*N*-phenylnitrone (**9b**) and **3**, 3-(2,4-dichlorobenzoyl)-8,8-dimethyl-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (**10b**) was prepared. Yield 50%; mp 69-70 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2\text{Cl}_2\text{S}$: C, 57.94; H, 4.63; N, 6.43; S, 7.35. Found: C, 58.05; H, 4.67; N, 6.51; S, 7.42. ^1H Nmr: 1.38, 1.52 (2 s, 6H, 2 CH_3), 2.22 (d, $J = 14.1$, 1H, $\text{H}_{\text{B-9}}$), 2.55 (dd, $J = 12.6$ and 5.1, 1H, $\text{H}_{\text{A-4}}$), 2.76 (d, $J = 14.1$, 1H, $\text{H}_{\text{A-9}}$), 3.45 (dd, $J = 12.6$ and 8.4, 1H, $\text{H}_{\text{B-4}}$), 5.48 (dd, $J = 8.4$ and 5.1, 1H, H-3), 6.99-7.43 (m, 8H, H_{arom}), 8.32 (br s, 1H, NH); ^{13}C nmr: 28.7, 28.8 (2 q, 2 CH_3), 41.4 (t, C-9), 49.1 (t, C-4), 61.6 (s, C-8), 72.3 (d, C-3), 92.4 (s, C-5), 115.8, 117.9, 122.7, 127.3, 128.5, 129.2, 130.3, 136.0, 137.6, 149.7 (C_{arom}), 199.0 (s, C=O), 201.5 (s, C=S).

8,8-Dimethyl-2,3-diphenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (10c)

C,*N*-Diphenylnitrone (**9c**) (1.972 g, 10 mmol) and **3** (1.412 g, 10 mmol) in dry toluene (50 ml) were heated under reflux for 36 h (tlc). Concentration under reduced pressure and chromatography using chloroform or hexane-ethyl acetate gave **10c**. Yield 2.033 g (60%); mp 196-197 °C. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{OS}$: C, 70.98; H, 6.55; N, 8.28; S, 9.46. Found: C, 70.85; H, 6.60; N, 8.12; S, 9.46. ^1H Nmr: 1.35, 1.51 (2 s, 6H, 2 CH_3), 2.13 (d, $J = 13.5$, 1H, $\text{H}_{\text{B-9}}$), 2.45 (dd, $J = 12.6$ and 8.7, 1H, $\text{H}_{\text{A-4}}$), 2.64 (d, $J = 13.5$, 1H, $\text{H}_{\text{A-9}}$), 3.43 (dd, $J = 12.6$ and 7.8, 1H, $\text{H}_{\text{B-4}}$), 5.07 (dd, $J = 8.7$ and

7.8, 1H, H-3), 6.93-7.49 (m, 10H, H_{arom}), 9.00 (br s, 1H, NH); ^{13}C nmr: 28.5, 28.9 (2 q, 2 CH_3), 49.4, 50.7 (2 t, C-4, C-9), 62.1 (s, C-8), 70.3 (d, C-3), 91.0 (s, C-5), 117.3, 122.7, 127.0, 127.7, 128.3, 128.8, 140.5, 150.3 (C_{arom}), 201.4 (s, C=S).

From *C*-(4-nitrophenyl)-*N*-phenylnitrone (**9d**) and **3**, 8,8-dimethyl-3-(4-nitrophenyl)-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (**10d**) was prepared. Yield 40%; mp 184-185 °C. Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3\text{S}$: C, 62.65; H, 5.52; N, 7.31; S, 8.35. Found: C, 62.61; H, 5.47; N, 7.29; S, 8.30. ^1H Nmr: 1.38, 1.54 (2 s, 6H, 2 CH_3), 2.15 (d, $J = 13.8$, 1H, $H_{\text{B-9}}$), 2.42 (dd, $J = 12.6$ and 8.7, 1H, $H_{\text{A-4}}$), 2.62 (d, $J = 13.8$, 1H, $H_{\text{A-9}}$), 3.49 (dd, $J = 12.6$ and 8.1, 1H, $H_{\text{B-4}}$), 5.28 (dd, $J = 8.7$ and 8.1, 1H, H-3), 6.94-7.27 (m, 9H, H_{arom}), 8.93 (br s, 1H, NH); ^{13}C nmr: 28.5, 28.8 (2 q, 2 CH_3), 49.1, 50.1 (2 t, C-4, C-9), 62.1 (s, C-8), 69.4 (d, C-3), 91.1 (s, C-5), 115.6, 117.1, 123.2, 124.05, 124.13, 127.8, 128.2, 128.5, 128.7, 147.5, 148.2, 149.8 (C_{arom}), 201.0 (s, C=S).

From *C*-phenyl-*N*-methylnitrone (**9g**) and **3**, 2,8,8-trimethyl-3-phenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (**10g**) was prepared. Yield 60%; mp 203-205 °C. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 65.21; H, 7.24; N, 10.14; S, 11.59. Found: C, 65.20; H, 7.44; N, 10.28; S, 11.63. ^1H Nmr: 1.35, 1.46 (2 s, 6H, 2 CH_3), 2.10 (d, $J = 13.5$, 1H, $H_{\text{B-9}}$), 2.35 (dd, $J = 12.6$ and 9.0, 1H, $H_{\text{A-4}}$), 2.61 (d, $J = 13.5$, 1H, $H_{\text{A-9}}$), 2.69 (s, 3H, NCH_3), 3.23 (dd, $J = 12.6$ and 6.9, 1H, $H_{\text{B-4}}$), 4.17 (dd, $J = 9.0$ and 6.9, 1H, H-3), 7.26-7.40 (m, 5H, H_{arom}), 8.19 (s, 1H, NH); ^{13}C nmr: 28.7, 28.9 (2 q, 2 CH_3), 43.6, 50.6 (2 t, C-4, C-9), 62.0 (s, C-8), 73.3 (d, C-3), 90.6 (s, C-5), 127.7, 128.0, 128.7, 138.3 (C_{arom}), 203.3 (s, C=S).

8,8-Dimethyl-3-(3-nitrophenyl)-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (**10e**).

8,8-Dimethyl-3-(3-nitrophenyl)-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonan-6-one (**12e**) (0.367 g, 1 mmol) and P_4S_{10} (2.223 g, 5 mmol) in dry pyridine (20 ml) were heated under reflux for 36 h (tlc). Concentration under reduced pressure and chromatography using chloroform-ethyl acetate gave **10e**. Yield 0.154 g (40%); mp 126-127 °C. Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3\text{S}$: C, 62.65; H, 5.52; N, 7.31; S, 8.35. Found: C, 62.68; H, 5.49; N, 7.17; S, 8.41. ^1H Nmr: 1.38, 1.54 (2 s, 6H, 2 CH_3), 2.17 (d, $J = 13.8$, 1H, $H_{\text{B-9}}$), 2.45 (dd, $J = 12.6$ and 9.0, 1H, $H_{\text{A-4}}$), 2.64 (d, $J = 13.8$, 1H, $H_{\text{A-9}}$), 3.48 (dd, $J = 12.6$ and 7.8, 1H, $H_{\text{B-4}}$), 5.28 (dd, $J = 9.0$ and 7.8, 1H, H-3), 6.97 - 8.40 (m, 9H, H_{arom}), 8.97 (br s, 1H, NH); ^{13}C nmr: 28.5, 28.8 (2 q, 2 CH_3), 49.1, 50.1 (2 t, C-4, C-9), 62.2 (s, C-8), 69.4 (d, C-3), 91.2 (s, C-5), 117.4, 121.9, 122.8, 123.3, 128.5, 129.8, 133.2, 142.9, 148.7, 149.7 (C_{arom}), 201.0 (s, C=S).

From 3-(4-methoxyphenyl)-8,8-dimethyl-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonan-6-one (**12f**) and P_4S_{10} , 3-(4-methoxyphenyl)-8,8-dimethyl-2-phenyl-1-oxa-2,7-diazaspiro[4.4]nonane-6-thione (**10f**) was prepared. Yield 33%; mp 189-190 °C. Anal. Calcd for $C_{21}H_{24}N_2O_2S$: C, 68.46; H, 6.56; N, 7.50; S, 8.68. Found: C, 68.50; H, 6.52; N, 7.63; S, 8.75. 1H Nmr: 1.36, 1.51 (2 s, 6H, 2 CH_3), 2.14 (d, $J = 14.1$, 1H, H_B-9), 2.43 (dd, $J = 12.3$ and 8.1, 1H, H_A-4), 2.65 (d, $J = 14.1$, 1H, H_A-9), 3.38 (dd, $J = 12.3$ and 7.8, 1H, H_B-4), 4.98 (dd, $J = 8.1$ and 7.8, 1H, H-3), 6.88-7.39 (m, 9H, H_{arom}), 8.91 (br s, 1H, NH); ^{13}C nmr: 28.6, 28.9 (2 q, 2 CH_3), 49.6, 50.8 (2 t, C-4, C-9), 55.3 (q, OCH_3), 62.1 (s, C-8), 70.2 (d, C-3), 90.8 (s, C-5), 114.2, 117.7, 122.9, 128.3, 132.1, 150.2, 159.2 (C_{arom}), 201.7 (s, C=S).

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