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

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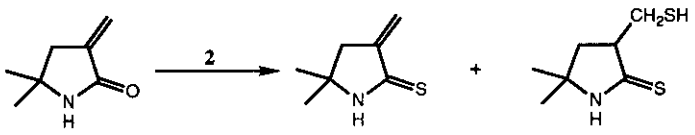
(Dedicated to Prof. Dr. Rolf Huisgen on the occasion of his 75th birthday)

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*-methylnitrone 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 synthetized by treatment of **6** with Lawesson´s reagent.

The concept of 1,3-dipolar cycloadditions[1] 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

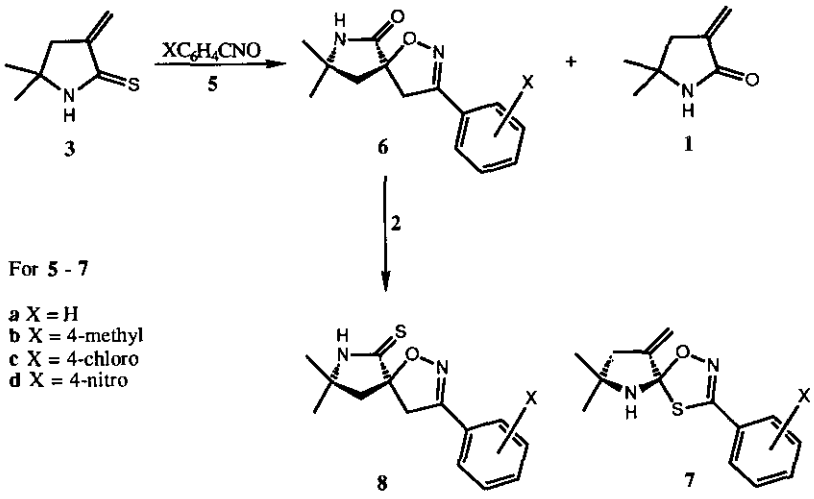
C=C double bonds, a small number of C=S double bonds have been used as dipolarophiles.[3,4] The recent observation of the strong herbicidal activity of spirocyclic lactams, coupled with the absence of toxicity to microorganisms[5] and also that some spiroisoxazolines occur naturally (Araplysillins are inhibitors of ATPase[6]) stimulated our interest in the synthesis of other spirocyclic derivatives. In a continuation of our efforts[7-10] to utilize heterocyclic compounds as dipolarophiles in 1,3-dipolar cycloaddition reactions, we have recently demonstrated that nitrones[7] and nitrile oxides[8] 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-methylene-pyrrolidine-2-thione (**3**), a dipolarophile possessing both a C=C as well as a C=S double bond.

The sulfurization of **1** with P_4S_{10} 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**).

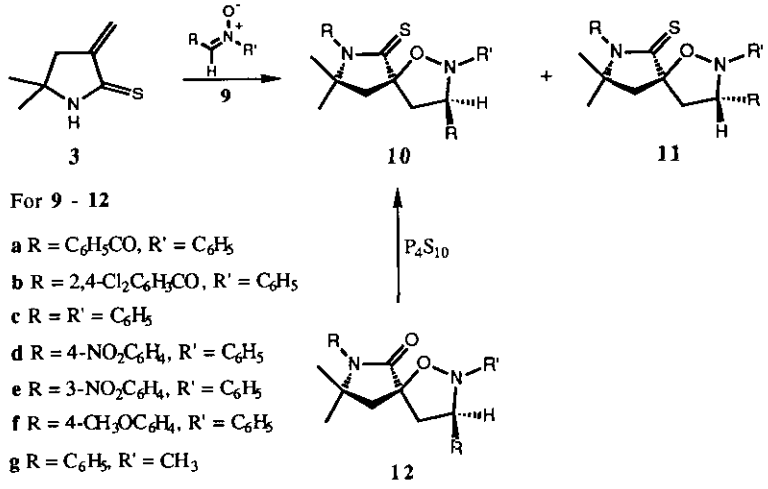


1 **3** **4**

The cycloaddition of thione (**3**) with arylnitrile 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 phenylisothiocyanate[4] 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, cycloadditons 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-NO_2 (**d**), 3-NO_2 (**e**), 4-CH_3O (**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 product[7] (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. ^{1}H 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. ^{1}H 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. ^{1}H 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 described[8] *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-CH_3 (**6b**, 45%), 4-Cl (**6c**, 67%) and 4-NO_2 (**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, 1mmol) 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 $C_{14}H_{16}N_2OS$: 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. ^{1}H Nmr: 1.42, 1.54 (2 s, 6H, 2 CH_3), 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}); ^{13}C nmr: 28.8 (q, 2 CH_3), 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 $C_{15}H_{18}N_2OS$: 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. ^{1}H Nmr: 1.41, 1.53 (2 s, 6H, 2 CH_3), 2.13 (d, J = 14.1, 1H, H_B-9), 2.38 (s, 3H, CH_3), 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}); ^{13}C nmr: 21.5 (q, CH_3), 28.8 (q, 2 CH_3), 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 $C_{14}H_{15}N_2OClS$: 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. ^{1}H Nmr: 1.42, 1.54 (2 s, 6H, 2 CH_3), 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); ^{13}C nmr: 28.8 (q, 2 CH_3), 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 $C_{14}H_{15}N_3O_3S$: 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. ^{1}H Nmr: 1.48, 1.52 (2 s, 6H, 2 CH_3), 2.18 (d, J = 12.0, 1H, H_B-9), 2.64 (d, J = 12.0, 1H, H_A-9), 3.23 (d, J = 17.1, 1H, H_A-4), 4.33 (d, J = 17.1, 1H, H_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 $C_{21}H_{22}N_2O_2S$: 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. ^{1}H Nmr: 1.34, 1.51 (2 s, 6H, 2 CH_3), 2.14 (d, J = 13.8, 1H, H_B-9), 2.62 (dd, J = 12.6 and 7.2, 1H, H_A-4), 2.66 (d, J = 13.8, 1H, H_A-9), 3.48 (dd, J = 12.6 and 8.4, 1H, H_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 $C_{21}H_{20}N_2O_2Cl_2S$: 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. ^{1}H Nmr: 1.38, 1.52 (2 s, 6H, 2 CH_3), 2.22 (d, J = 14.1, 1H, H_B-9), 2.55 (dd, J = 12.6 and 5.1, 1H, H_A-4), 2.76 (d, J = 14.1, 1H, H_A-9), 3.45 (dd, J = 12.6 and 8.4, 1H, H_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 $C_{20}H_{22}N_2OS$: 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. ^{1}H Nmr: 1.35, 1.51 (2 s, 6H, 2 CH_3), 2.13 (d, J = 13.5, 1H, H_B-9), 2.45 (dd, J = 12.6 and 8.7, 1H, H_A-4), 2.64 (d, J = 13.5, 1H, H_A-9), 3.43 (dd, J = 12.6 and 7.8, 1H, H_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 $C_{20}H_{21}N_3O_3S$: 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_B-9), 2.42 (dd, J = 12.6 and 8.7, 1H, H_A-4), 2.62 (d, J = 13.8, 1H, H_A-9), 3.49 (dd, J = 12.6 and 8.1, 1H, H_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 $C_{15}H_{20}N_2O_2S$: 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_B-9), 2.35 (dd, J = 12.6 and 9.0, 1H, H_A-4), 2.61 (d, J = 13.5, 1H, H_A-9), 2.69 (s, 3H, NCH_3), 3.23 (dd, J = 12.6 and 6.9, 1H, H_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 $C_{20}H_{21}N_3O_3S$: 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_B-9), 2.45 (dd, J = 12.6 and 9.0, 1H, H_A-4), 2.64 (d, J = 13.8, 1H, H_A-9), 3.48 (dd, J = 12.6 and 7.8, 1H, H_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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