# A CONVENIENT SYNTHESIS OF 5-SUBSTITUTED TETRAHYDRO-1,4,3-OXATHIAZINE 4,4-DIOXIDES

Evelyne Grunder-Klotz *, Paul Humbert, and Jean-Daniel Ehrhardt

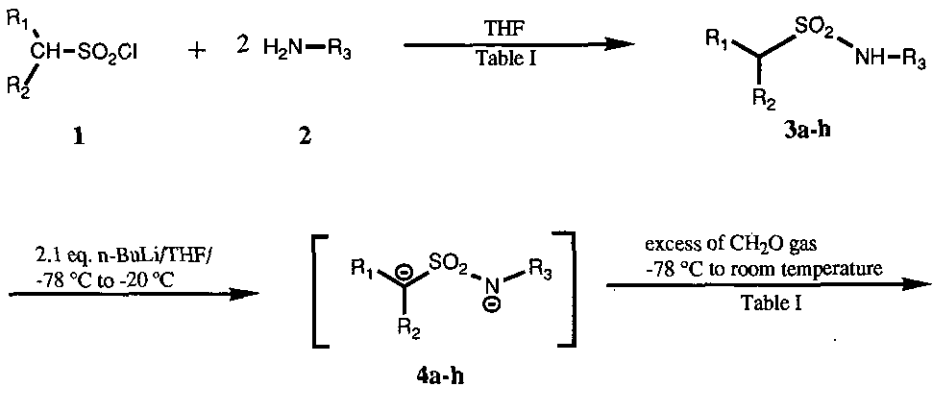
Laboratoire de Pharmacologie Cardiovasculaire et Rénale, URA 589 CNRS, Université Louis Pasteur, 11 rue Humann, 67000 Strasbourg, France

**Abstract**- An advantageous one pot procedure for the synthesis of tetrahydro-1,4,3-oxathiazine 4,4-dioxides by dialkylation of readily available α,*N*-alkyl- or arylsulfonamide dianions with gaseous formaldehyde is reported. Stability and some reactions of these heterocycles are also described.

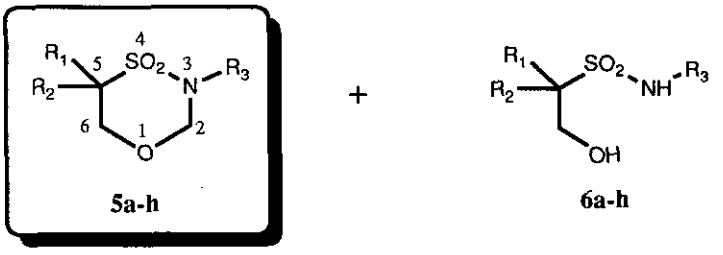
Recently, many sulfonamides or heterocycles containing a sulfonamide moiety have been described in the literature.[1-2] They are considered attractive synthetic targets to identify new biologically active compounds. These reports prompted us to develop our own findings in this field, particularly the synthesis of tetrahydro-1,4,3-oxathiazine 4,4-dioxides (abrev. THOx), a six membered heterocycle containing a sulfonamide function.[3]

*In this publication, we wish to demonstrate the application of our new method of THOx preparation and* some of its steric and electronic limitations. Stability studies and some reactions of these heterocycles are also reported.

Simple α,*N*-alkyl- or alrylsulfonamides (**3**) are obtained by treatment of alkylsulfonyl chlorides (**1**) with two equivalents of the appropriate amines (**2**) in dry THF (Scheme 1).




1 2 3a-h 4a-h



5a-h 6a-h

| Products | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| a | H | H | 4-$ClC_6H_4$ |
| b | H | H | 4-$CH_3OC_6H_4$ |
| c | H | H | $CH_2C_6H_5$ |
| d | $CH_3$ | H | $CH_2C_6H_5$ |
| e | $CH_3$ | $CH_3$ | $CH_2C_6H_5$ |
| f | $C_6H_5$ | H | $CH_2C_6H_5$ |
| g | $C_6H_5$ | H | $(CH_2)_3CH_3$ |
| h | $C_6H_5$ | H | $CH(CH_3)_2$ |

**Scheme 1**

These readily available compounds (**3**) are then reacted with 2.1 equivalents of n-BuLi in dry THF at -78 °C to -20 °C to form dianions (**4**). These reactive intermediates are then treated with a large excess of gaseous formaldehyde (obtained by cracking paraformaldehyde at 165 °C). After acidic work-up and purification, we isolate new THOx, (**5a-h**), in 15 to 60% yield (Table I). As observed by thin layer chromatography (tlc) and mass spectroscopy of the crude reaction mixtures, some alcohols (**6a-h**) were always present in the reactions. These alcohols result from monoalkylation of dianions (**4**).[4] The physical constants of compounds (**5a-h**) are listed in Table II and Table III.

**Table I.** Yields of compounds (**3** and **5**)

| Compounds | Yield (%) | Compounds | Yield (%) |
|---|---|---|---|
| **3 a** | 80 | **5 a** | 15 |
| **3 b** | 95 | **5 b** | 60 |
| **3 c** | 90 | **5 c** [a] | 55 |
| **3 d** | 95 | **5 d** | 50 |
| **3 e** | 75 | **5 e** | 40 |
| **3 f** | 75 | **5 f** | 60 |
| **3 g** | 80 | **5 g** | 50 |
| **3 h** | 90 | **5 h** | 30 |

a) This compound is reported in the literature. See Ref. 6.

**Table II.** Tetrahydro-1,4,3-Oxathiazine 4,4-Dioxides (**5a-h**)

| Compound | mp (°C) [a] (Solvent) | ir ($cm^{-1}$) ($CHCl_3$ or $CCl_4$) | ms (m/z, %) |
|---|---|---|---|
| **5 a** | 93 (petroleum ether) | 1355, 1160 ($SO_2$), 1075 ($SO_2$) | 247/249 (93, $M^{+\cdot}$); 217/219 (23, $[M-30]^+$); 139/141 (50, $[CH_2=N(C_6H_4Cl)]^{+\cdot}$); 138/140 (58, $[CH=N(C_6H_4Cl)]^+$); 125/127 (100, $[N(C_6H_4Cl)]^+$); 111/113 (24, $[C_6H_4Cl]^{+\cdot}$) |
| **5 b** | 108 (hexane/AcOEt:7/3) | 1350, 1155 ($SO_2$), 1070 ($SO_2$) | 243 (100, $M^{+\cdot}$); 179 (32, $[M-(SO_2)]^{+\cdot}$); 178 (52, $[M-(SO_2)-(H)]^+$); 164 (38, $[M-(SO_2)-(CH_3)]^+$); 149 (21, $[M-(SO_2)-(CH_2O)]^{+\cdot}$); 134 (48, $[M-(SO_2)-(CH_2O)-(CH_3)]^+$); 121 (64); 120 (34) |
| **5 c** | 87-88 (cyclohexane) | 1360, 1160 ($SO_2$), 1120 ($SO_2$), 910 | 227 (15, $M^{+\cdot}$); 163 (2, $[M-(SO_2)]^{+\cdot}$); 162 (3, $[M-(SO_2)-(H)]^+$); 134 (31); 118 (24, $[Ph-CH=N=CH_2]^+$); 104 (13); 91 (100, $[PhCH_2]^+$) |
| **5 d** | 98-99 (hexane) | 1350, 1160 ($SO_2$), 1115 ($SO_2$), 900 | 241 (8, $M^{+\cdot}$); 177 (4, $[M-(SO_2)]^{+\cdot}$); 176 (3, $[M-(SO_2)-(H)]^+$); 150 (4, $[M-(CH_2Ph)]^+$); 147 ($[M-(SO_2)-(CH_2O)]^{+\cdot}$); 135 (18); 134 (23); 118 (30, $[PhCH=N=CH_2]^+$); 91 (100, $[PhCH_2]^+$) |
| **5 e** | 103-104 (hexane) | 1330, 1150 ($SO_2$), 1060 ($SO_2$), 905 | 255 (3, $M^{+\cdot}$); 135 (4); 120 (6); 118 (32, $[PhCH=N=CH_2]^+$); 92 (20); 91 (100, $[PhCH_2]^+$) |
| **5 f** | 134-135 (cyclohexane) | 1350, 1160 ($SO_2$), 1050 ($SO_2$), 900 | 303 (2, $M^{+\cdot}$); 239 (9, $[M-(SO_2)]^{+\cdot}$); 238 (16, $[M-(SO_2)-(H)]^+$); 209 (7, $[M-(SO_2)-(CH_2O)]^{+\cdot}$); 208 (5, $[M-(SO_2)-(H)-(CH_2O)]^+$); 148 (7); 118 (28); 105 (16); 91 (100, $[PhCH_2]^+$) |
| **5 g** | 79 (hexane) | 1345, 1150 ($SO_2$), 1080 ($SO_2$), 905 | 269 (16, $M^{+\cdot}$); 239 (6, $[M-(CH_2O)]^{+\cdot}$); 226 (6, $[M-(CH_2CH_2CH_3)]^+$); 205 (11, $[M-(SO_2)]^{+\cdot}$); 204 (6, $[M-(SO_2)-(H)]^+$); 175 (6, $[M-(SO_2)-(CH_2O)]^{+\cdot}$); 174 (6, $[M-(SO_2)-(CH_2O)-(H)]^+$); 163 (13); 162 (100, $[M-(SO_2)-(CH_2CH_2CH_3)]^{+\cdot}$); 133 (12); 132 (9, $[M-(SO_2)-(CH_2CH_2CH_3)-(CH_2O)]^+$); 104 (26); 91 (26, $[PhCH_2]^+$); 86 (19); 84 (25) |
| **5 h** | 90-91 [b] | 1350, 1150 ($SO_2$), 1080 ($SO_2$), 920 | 255 (10, $M^{+\cdot}$); 240 (8, $[M-(CH_3)]^+$); 225 (5, $[M-(CH_2O)]^{+\cdot}$); 191 (11, $[M-(SO_2)]^{+\cdot}$); 190 (4, $[M-(SO_2)-(H)]^+$); 177 (10); 176 (57, $[M-(CH_3)-(SO_2)]^+$); 161 (5, $[M-(CH_2O)-(SO_2)]^{+\cdot}$); 160 (11, $[M-(CH_2O)-(SO_2)-(H)]^+$); 146 (7, $[M-(CH_2)-(SO_2)-(CH_3)]^+$); 119 (7); 104 (28); 103 (15); 91 (27, $[PhCH_2]^+$); 72 (20); 56 (100) |

a) Values are given ± 2 °C
b) After double silica gel column chromatography.

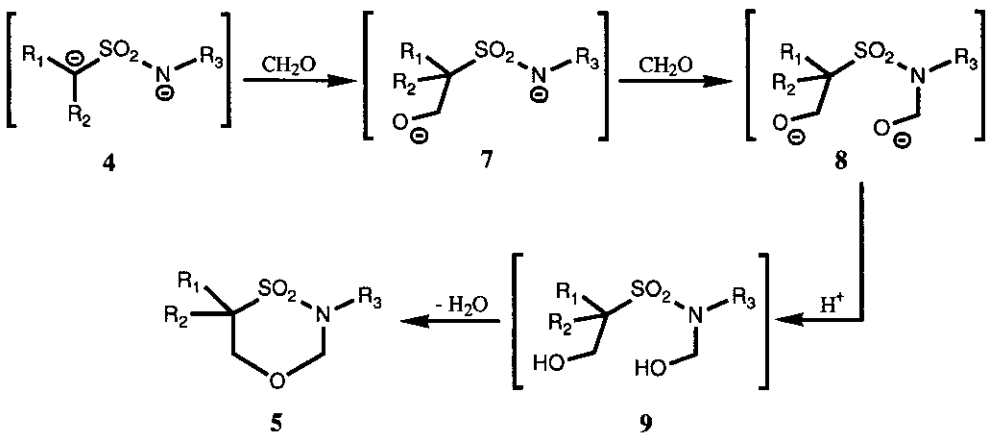
**Table III.** Nmr data of compounds (**5a-h**)

| Compound | $^1$H-nmr (200 MHz, $CDCl_3$) δ (ppm), *J* (Hz) | $^{13}$C-nmr (50 MHz, $CDCl_3$) δ (ppm) |
|---|---|---|
| **5 a** | 3.19-3.25 (2H, m, $CH_2SO_2$), 4.39-4.44 (2H, m, $CH_2O$), 5.31 (2H, s, $OCH_2N$), 7.32-7.38 ($2H_{arom.}$, syst. AA'XX', AA' part, *J* = 10.6), 7.45-7.52 ($2H_{arom.}$, syst. AA'XX', XX' part, *J* = 9.8) | 48.59 ($CH_2$), 66.30 ($CH_2$), 83.48 ($CH_2$), 127.34-169.19 ($CH_{arom.}$), 133.43 and 139.49 ($C_{arom.}$) |
| **5 b** | 3.20-3.25 (2H, m, $CH_2SO_2$), 3.80 (3H, s, $OCH_3$), 4.38-4.43 (2H, m, $CH_2O$), 5.28 (2H, s, $OCH_2N$), 6.84-6.92 ($2H_{arom.}$, syst. AA'XX', AA' part, *J* = 9.0), 7.04-7.50 ($2H_{arom.}$, syst. AA'XX', XX' part, *J* = 10.2) | 48.35 ($CH_2$), 55.50 ($CH_3$), 66.33 ($CH_2$), 83.92 ($CH_2$), 114.32-127.70 ($CH_{arom.}$), 133.94 and 159.03 ($C_{arom.}$) |
| **5 c** | 3.21-3.26 (2H, m, $CH_2SO_2$), 4.23-4.28 (2H, m, $CH_2O$), 4.47 (2H, s, $CH_2N$), 4.78 (2H, s, $OCH_2N$), 7.33-7.40 ($5H_{arom.}$, m) | 48.05 ($CH_2$), 51.36 ($CH_2$), 65.99 ($CH_2$), 80.07 ($CH_2$), 128.15-128,80 ($CH_{arom.}$), 135.40 ($C_{arom.}$ |
| **5 d** | 1.35 (3H, d, *J* = 6.4, $CH_3$), 3.36 (1H, m, $CHSO_2$), 3.73-4.13 (2H, m, $CH_2O$), 4.54-4.95 (4H, m, $CH_2N$ and $OCH_2N$), 7.34-7.39 ($5H_{arom.}$, m) | 9.32 ($CH_3$), 51.35 (CH), 53.79 ($CH_2$), 71.60 ($CH_2$), 80.02 ($CH_2$), 128.09-128.76 ($CH_{arom.}$), 135.70 ($C_{arom.}$) |
| **5 e** | 1.47 (6H, s, 2 $CH_3$), 3.66 (2H, s, $CH_2O$), 4.54 (2H, s, $CH_2N$), 4.76 (2H, s, $OCH_2N$), 7.27-7.36 ($5H_{arom.}$, m) | 9.76 ($CH_3$), 53.11 (CH), 59.75 ($CH_2$), 76.67 ($CH_2$), 80.62 ($CH_2$), 127.92-128.73 ($CH_{arom.}$), 136.78 ($C_{arom.}$) |
| **5 f** [a] | 4.24-5.13 (7H, m, $CHSO_2$, $CH_2O$, $CH_2N$ and $OCH_2N$), 7.30-7.50 ($10H_{arom.}$, m) | 51.57 ($CH_2$), 63.68 (CH), 70.82 ($CH_2$), 79.93 ($CH_2$), 128.18-135.52 ($CH_{arom.}$ and $C_{arom.}$) |
| **5 g** | 0.95 (3H, t, $CH_3$), 1.25-1.87 (4H, m, $CH_2$-$CH_2$), 3.22-3.59 (2H, m, $CH_2N$), 4.19-4.43 (3H, m, $CHSO_2$ and $CH_2O$), 4.78-5.23 (2H, m, $OCH_2N$), 7.26-7.47 ($5H_{arom.}$, m) | 13.57 ($CH_3$), 19.74 ($CH_2$), 31.26 ($CH_2$), 48.33 ($CH_2$), 63.72 (CH), 70.62 ($CH_2$), 81.20 ($CH_2$), 128.96-129.50 ($CH_{arom.}$ and $C_{arom.}$) |
| **5 h** | 1.28 (3H, d, *J* = 6.8, $CH_3$), 1.40 (3H, d, *J* = 6.8, $CH_3$), 4.17-4.45 (4H, m, $CH_2O$, $CHSO_2$ and NCH), 4.93-5.17 (2H, m, $OCH_2N$), 7.36-7.45 ($5H_{arom.}$, m) | 21.87 ($CH_3$), 22.82 ($CH_3$), 50.17 ($CH_2$), 66.66 (CH), 71.11 ($CH_2$), 77.03 ($CH_2$), 128.93-129.77 ($CH_{arom.}$ and $C_{arom.}$) |

a) $^1$H Nmr spectra were taken at 400 MHz

It seems likely that the ease of formation of THOx is dependent on the steric bulk of the starting sulfonamide (**3**) and on the basicity of its NH group. Indeed, an increase of the steric hindrance at position 3 (**5g**, **5h**) or 5 (**5c-e**) diminishes the yield of the products. These observations are in accordance with our previous results (see ref. 3), demonstrating that the steric bulk of the electrophile (aldehyde) used influence also the yield of the reaction. On the other hand, the reactivity of the $N^-$ anion in intermediate (**4**) seems also crucial for the dialkylation of these dianions. As shown in Table I, the yield of **5b**, where the phenyl moiety is substituted by an electron-donating group (OMe) is higher than that of **5a**, with an electron-withdrawing group (Cl) on the phenyl ring.

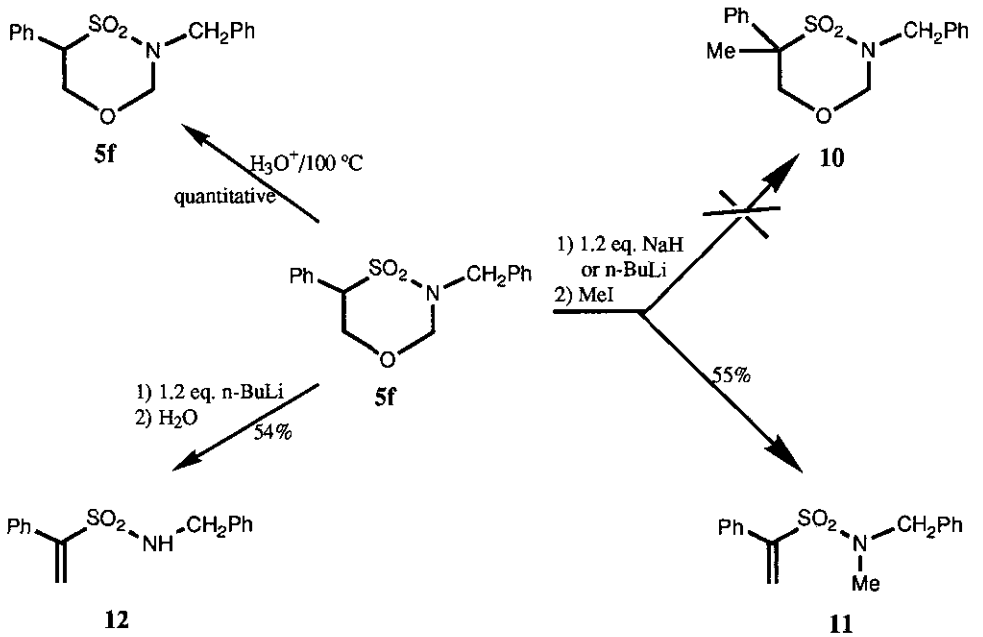
In view of these and our earlier results (see ref. 3), we can postulate a mechanism as described in the Scheme 2. After formation of the dianion (**4**), the carbanion is alkylated first by one molecule of $CH_2O$ yielding intermediate (**7**), followed by the alkylation of the nitrogen anion to form an intermediate presumably like (**8**). This is due to the large excess of $CH_2O$ always present in the reaction mixture (cracking paraformaldehyde) and, of the very small steric bulk of $CH_2O$. During the acidic work-up, protonation gives diol (**9**), which is dehydrated to obtain the thermodynamically stable six membered cyclic compounds (**5**).




**Scheme 2**

We were then interested in studying the chemical stability and reactivity of these heterocycles.[6] These results are summarized in the Scheme 3. Compound (**5f**) is stable in hot acidic solution and is completely recovered after 24 h of reaction. We were not able to methylate compound (**5f**) in position 5 to obtain compound (**10**). Treatment of the compound (**5f**) with a base (NaH/room temperature or n-BuLi/-78 °C) followed by either MeI or water resulted in the exclusive formation of (**11**) or (**12**) respectively. In order, to synthesize highly substituted heterocycles, one therefore has to start with the correctly substituted sulfonamides [e.g. (**3e**) and (**5e**)].

Compounds (**11**) and (**12**) contain an activated electrophilic ethenesulfonamide group. They are described as useful intermediates in the manufacture of dyes, pesticides, synthetic resins and textile auxiliary agents.[7, 8] These results would open new applications of ethenesulfonamides and THOx in industrial chemistry.




**Scheme 3**

In conclusion, our experiments indicate that within the limits discussed in this paper, tetrahydro-1,4,3-oxathiazine 4,4-dioxides can be easily prepared. Moreover, this is the first synthetic method described to obtain 5-substituted tetrahydro-1,4,3-oxathiazine 4,4-dioxides.

## EXPERIMENTAL SECTION

Melting points were taken using a Gallenkamp apparatus and are corrected. Elemental analysis were performed by the "Service de Microanalyses du CNRS" at the "Institut de Chimie", Strasbourg. Mass spectra were recorded on a LKB 2091 spectrometer. Ir spectra were run on a Philips PU 9716 spectrophotometer. $^{1}$H-Nmr spectra were obtained either on a Bruker WP200SY (200 MHz) or on a Bruker AM400 (400 MHz) spectrometer. $^{13}$C Nmr were recorded on a Bruker WP200SY (50 MHz) spectrometer. α,*N*-Alkyl- or arylsulfonamides (**3a-h**) were synthesized using a standard procedure described in ref. 4. Yields (Table I) refer to spectroscopically homogeneous materials. All air sensitive experiments were carried out under argon atmosphere and with freshly dried, distilled (Na/benzophenone) THF.

**Tetrahydro-1,4,3-oxathiazine 4,4-dioxides (5a-h); general procedure.** To a solution of α,*N*-alkyl- or arylsulfonamide (**3a-h**) (300 mg) in dry THF (10 ml) at -78 °C is added dropwise a solution of 1.6M n-BuLi in hexane [2.1 eq. n-BuLi/(**3**)]. The mixture was stirred for about 2 h at -78 °C to -20 °C. The dianion solution is recooled to -78 °C and gaseous formaldehyde (generated by cracking a large excess of paraformaldehyde at 165 °C; 5.20 g) was bubbled through the mixture. After stirring at room temperature for approximately 12 h, 12% aqueous HCl (5 ml) is added. After filtration of the reaction mixture, the solvents were removed under reduced pressure. The crude product is purified by silica gel column chromatography with $CH_2Cl_2$ or Hex/AcOEt in variable concentrations as eluent. Physical data of compounds (**5a-h**) are reported in Tables II and III.

3-(4-Chlorophenyl)tetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5a**). Anal. Calcd for $C_9H_{10}NO_3ClS$: C, 43.64; H, 4.07; N, 5.65. Found: C, 43.48; H, 4.05; N, 5.60.

3-(4-Methoxyphenyl)tetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5b**). Anal. Calcd for $C_{10}H_{13}NO_4S$: C, 49.37; H, 5.38; N, 5.75. Found: C, 49.19; H, 5.18; N, 5.72.

3-Benzyltetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5c**). Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.94; H, 5.81; N, 6.08.

3-Benzyl-5-methyltetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5d**). Anal. Calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80. Found: C, 54.55; H, 6.25; N, 5.74.

3-Benzyl-5,5'-dimethyltetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5e**). Anal. Calcd for $C_{12}H_{17}NO_3S$: C, 56.44; H, 6.71; N, 5.49. Found: C, 56.36; H, 6.76; N, 5.43.

3-Benzyl-5-phenyltetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5f**). Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.35; H, 5.65; N, 4.62. Found: C, 63.22; H, 5.54; N, 4.61.

3-nButyl-5-phenyltetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5g**). Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.10; N, 5.20. Found: C, 57.96; H, 6.99; N, 5.22.

3-Isopropyl-5-phenyltetrahydro-1,4,3-oxathiazine 4,4-dioxide (**5h**). Anal. Calcd for $C_{12}H_{17}NO_3S$: C, 56.44; H, 6.79; N, 5.49. Found: C, 56.70; H, 6.77; N, 5.42.

***N*-Methyl-*N'*-benzyl-1-phenylethenylsulfonamide (11).** To a solution of **5f** (57 mg, 0.19 mmol) in dry THF (8 ml) NaH (20% in oil, 29 mg, 0.24 mmol) or n-BuLi (1.6M/hexane, 0.14 ml, 0.20 mmol) was added. After stirring at room temperature (when we used NaH), or at -78 °C (when we used n-BuLi), under argon for 2 h, MeI (0.12 ml, 1.9 mmol) was added to the solution. The resulting mixture was stirred at room temperature for 24 h, then the precipitate was filtered and the filtrate's solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography with hexane/AcOEt: 85/15 as eluent. An oil, **11**, was obtained in 30 mg (55%).

$^1$H Nmr (200 MHz, $CDCl_3$) δ: 2.50 (3H, s, $NCH_3$), 3.96 (2H, s, $NCH_2$), 5.91 (1H, s, CH=C), 6.40 (1H, s, CH=C), 7.16-7.60 ($10H_{arom}$, m); ir ($CHCl_3$) ν: 1320, 1140, 975, 920 cm$^{-1}$; ms, m/z (relative intensity): 287 (14, $M^{+\cdot}$); 223 (4, $[M-(SO_2)]^{+\cdot}$); 222 (14, $[M-(SO_2)-(H)]^+$); 120 (85, $[Ph-CH=NHCH_3]^+$); 103 (100, $[Ph-C=CH_2]^+$); 91 (36, $[PhCH_2]^+$); 77 (30, $[Ph]^+$). Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.55; H, 5.82; N, 4.69.

***N*-Benzyl-1-phenylethenylsulfonamide (12).** To a solution of **5f** (25 mg, 0.08 mmol) in dry THF (5 ml) was added n-BuLi (1.6M/hexane, 0.06 ml, 0.09 mmol). After stirring at -78 °C under argon for 2 h, $H_2O$ (50 µl) was added to the solution. The resulting mixture was stirred at room temperature for 4 h, then the precipitate was filtered and the solvent's filtrate was evaporated in vacuo. The residue was purified by silica gel column chromatography with $CH_2Cl_2$ as eluent. An oil, **12**, was obtained in 12 mg (54%).$^1$H Nmr (200 MHz, $CDCl_3$) δ: 4.07-4.10 (2H, d, J=6.0 Hz, $\mathbf{CH_2}$N), 4.33 (1H, br s, **NH**), 5.93 (1H, s, CH=C), 6.44 (1H, s, CH=C), 7.14-7.57 (10$\mathbf{H_{arom}}$, m); ms, m/z (relative intensity): 273 (4, $M^{+\cdot}$); 209 (6, $[M-(SO_2)]^{+\cdot}$); 208 (8, $[M-(SO_2)-(H)]^+$); 106 (72, $[PhCH=NH_2]^+$); 103 (100, $[Ph-C=CH_2]^+$); 91 (37, $[PhCH_2]^+$); 77 (33, $[Ph]^+$).

## REFERENCES


1 M. E. Thompson, *Synthesis* , 1988, 733; T. J. Ward, G. J. Warrellow, J. A. Stirrup, N. Lattimer, and K. F. Rhodes, *J. Med. Chem.*, 1989, **32**, 179; J. H. Musser, A. F. Kreft, R. H. W. Bender, D. M. Kubrak, R. P. Carlson, J. Chang, and J.-M. Hand, *J. Med. Chem.*, 1989, **32**, 1176; C.Subranyam and M. R. Bell, *Bioorg. & Med. Chem. Lett.*, 1991, **1**, 733; T. Iwakawa, H. Tamura, A. Murabayashi, and Y. Hayase, *Chem. Pharm. Bull.*, 1991, **39**, 1939; S. Mignani, C. Gueremy, J.-L. Malleron, A. Truchon, J.-F. Peyronel, and J.-P. Bastart, *Heterocycles*, 1992, **34**, 907.

2 For example of antiinflammatory and anxiolytic sulfonamide compounds in clinical tests see: *Drugs Fut.*, 1991, **16**, 164 and *Drugs Fut.*, 1991, **16**, 661.

3 E. Grunder-Klotz and J.-D. Ehrhardt, *Synlett*, 1991, 800.

4 M. E. Thompson, *J. Org. Chem.*, 1984, **49**, 1700.

5 L. Rodriguez, N. Lu, and N.-L. Yang, *Synlett*, 1990, 227.

6 Only few oxathiazines are described in the literature see: F. Meininger, *Ind. Chim. Belge*, 1967, **32** (Spec. N°) 76, (*Chem. Abstr.*, 1967, **70**, 79112q).

7 A. LeBerre and C. Porte, *Bull. Soc. Chim. Fr.*, 1976, 602.

8 G. Lange, F. Ebel, R. Schroedel, and W. Hensel, Brit Patent 875946 (1961), (*Chem. Abstr.*, 1962, **59**, 7687d).


Received, 14th August, 1992