

## 4-Methyl-N-(2,2,4,4-tetrachloro-5-methyl-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-1-ylmethyl)-benzenesulfonamide

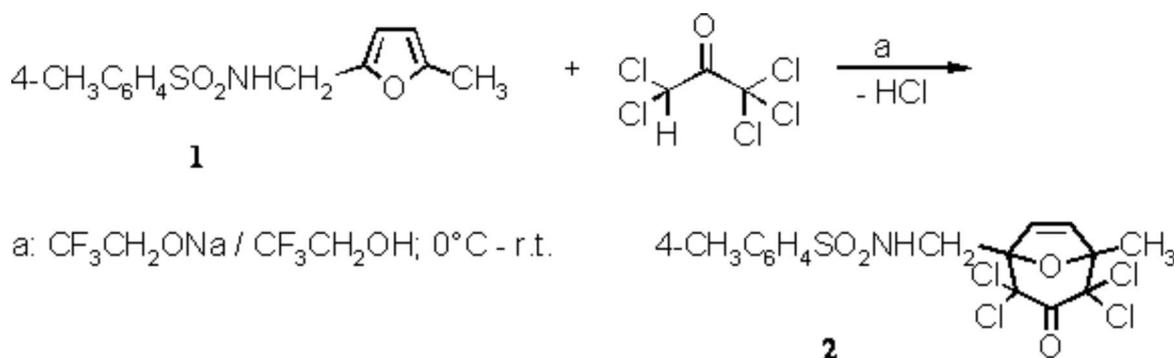
Holger Meining and Baldur Föhlisch\*

Institut für Organische Chemie der Universität Stuttgart,  
Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Fax: (+ 49) 711/6854269; e-mail: [baldur.foehlich@oc.uni-stuttgart.de](mailto:baldur.foehlich@oc.uni-stuttgart.de)

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A mixture of **1** [1] (2.65 g, 10 mmol) and pentachloroacetone [2] (3.23 g, 14 mmol) was cooled in an ice bath. With magnetic stirring, a 2-molar solution of sodium 2,2,2-trifluoroethoxide in 2,2,2-trifluoroethanol [3] (7 mL, 14 mmol) was added dropwise, over 15 min. Stirring was continued for 15 min at 0 °C and then at room temperature for 2–3 hours[4]. The mixture was allowed to stir for a further 2 hours.

The heterogeneous mixture was poured on saturated brine (20 mL). The precipitate was dissolved by adding a little of dichloromethane and water, and the organic layer was separated. The aqueous layer was acidified with hydrochlorid acid to pH 4–5 and then extracted with dichloromethane (4 × 20 mL). The combined dichloromethane solutions were washed with saturated brine (20 mL) and dried overnight with magnesium sulfate. After filtration, the solution was concentrated in a rotary evaporator. The remaining yellow mass was recrystallized from dry ethanol (60 mL) to yield 4.01 g (87%) of **2** as a colourless crystalline solid.

Melting Point: 177–178 °C.

TLC (silica, hexane/*tert*-butylmethyl ether (1:1 v/v): A light-blue spot emerged after spraying the sheet with vanillin/sulfuric acid reagent followed by heating with a hot-air gun;  $R_f = 0.31$ . The starting material (**1**) showed a red-brown spot at  $R_f = 0.38$ .

$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.75$  (s, 3 H, 5- $\text{CH}_3$ ); 2.45 (s, 3 H,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ); ABX sub-spectrum (8 AB-lines, X part as a broad m) with  $\delta_A = 3.89$ ,  $\delta_B = 3.58$ ,  $\delta_X = 4.88$ ,  $J_{AB} = (-) 13.9$  Hz,  $J_{AX} = 10.1$  Hz,  $J_{BX} = 3.3$  Hz, 3 H, diastereotopic  $\text{CH}_2\text{-NH}$ ); 6.34 (s, 2 H, H-7 + H-6); AA'BB' sub-spectrum with  $\delta_A = 7.76$ ,  $\delta_B = 7.35$ ,  $J_{AB} = 8.2$  Hz (H-2/6 and H-3/5 from  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ).

$^1\text{H-NMR}$  (250 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 1.65$  (s, 3 H, 5- $\text{CH}_3$ ); 2.39 (s, 3 H,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ); ABX sub-spectrum (8 AB-lines, 4 lines of the X part) with  $\delta_A = 3.63$ ,  $\delta_B = 3.44$ ,  $\delta_X = 8.06$ ,  $J_{AB} = (-) 14.4$  Hz,  $J_{AX} = 7.5$  Hz,  $J_{BX} = 5.7$  Hz, 3 H, diastereotopic  $\text{CH}_2\text{-NH}$ ); 6.46 (d,  $J = 5.8$  Hz, 1 H, H-7); 6.66 (d,  $J = 5.8$

Hz, 1 H, H-6); AA'BB' sub-spectrum with  $\delta_A = 7.76$ ,  $\delta_B = 7.36$ ,  $J_{AB} = 8.0$  Hz (H-2/6 and H-3/5 from  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ).

$^{13}\text{C}$ -NMR/DEPT (62.9 MHz, DMSO- $d_6$ ):  $\delta = 16.2$  (+, 5- $\text{CH}_3$ ); 20.9 (+,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ); 41.9 (-,  $\text{CH}_2\text{-N}$ ); 84.7 ( $\text{C}_q$ , C-4); 87.1 ( $\text{C}_q$ , C-2); 91.2 ( $\text{C}_q$ , C-5); 92.7 ( $\text{C}_q$ , C-1); 126.35 (+, C-2/6 from  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ -); 129.65 (+, C-3/5 from  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ); 134.6 (+, C-6); 137.6 ( $\text{C}_q$ , C-4 from  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ); 138.0 (+, C-7); 142.85 ( $\text{C}_q$ , C-1 from  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ); 185.3 ( $\text{C}_q$ , C-3).

IR ( $\text{CHCl}_3$  film,  $\text{cm}^{-1}$ ): 3400 (N-H); 3110, 2960 (C-H); 1773, 1745 (C=O); 1600 (C=C); 1495 (NH); 1340, 1165  $\text{cm}^{-1}$  ( $\text{SO}_2$ ).

Elemental Analysis: Calculated for  $\text{C}_{16}\text{H}_{15}\text{Cl}_4\text{NO}_4\text{S}$  (459.2): C, 41.85%; H, 3.29%; Cl, 30.88%; N, 3.05%; S, 6.98%. Found: C, 41.59%; H, 3.23%; Cl, 30.75%; N, 2.91%; S, 7.03%.

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4. If **1** has not disappeared after that time (check by TLC), more pentachloroacetone (0.7–1.2 g, 3–5 mmol) was added, and the base solution in such amount that a test with wet pH indicator paper showed an alkaline reaction.

*Sample Availability:* Available from MDPI.

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