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

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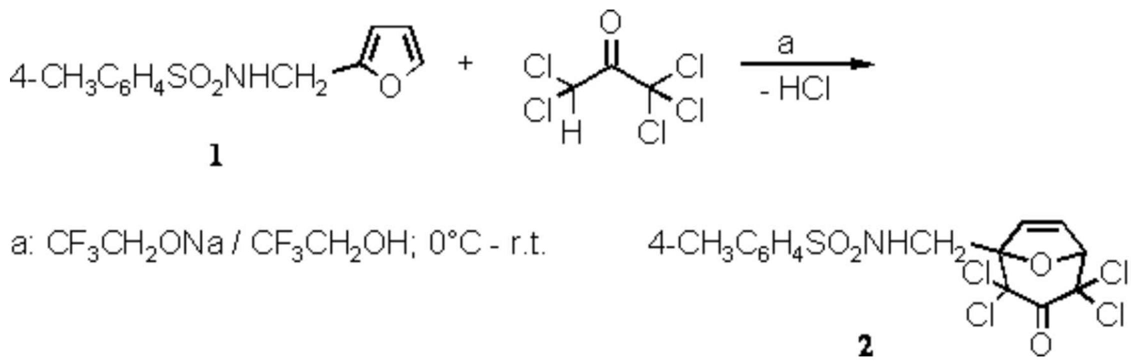

A mixture of *N*-furfuryl-*p*-toluenesulfonamide (**1**) (2.51 g, 10 mmol) [1] and pentachloroacetone [2] (3.23 g, 14 mmol) was cooled in an ice bath. With magnetic stirring, a 2-molar solution of sodium 2,2,2-trifluoroethoxide in 2,2,2-trifluoroethanol[3] (7 mL, 14 mmol) was added dropwise, over 15 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. Then, 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 (10 mL) to yield 3.60 g (81%) of **2** as a colourless crystalline solid.

Melting Point: 162–163 °C.

TLC (silica, hexane/*tert*-butylmethyl ether (1:1 v/v): A pale yellow spot emerged after spraying the sheet with vanillin/sulfuric acid reagent followed by heating with a hot-air gun; $R_f = 0.27$. The starting material (**1**) showed a brownish violet spot at $R_f = 0.37$.

^{1}H-NMR (250 MHz, $CDCl_3$): δ= 2.45 (s, 3 H, $CH_3C_6H_4SO_2$); ABX sub-spectrum (14 lines) with $\delta_A = 3.89$, $\delta_B = 3.65$, $\delta_X = 5.10$, $J_{AB} = (-)14$ Hz, $J_{AX} = 9.6$ Hz, $J_{BX} = 3.6$ Hz, 3 H, diastereotopic CH_2-NH); 5.16 (d, $J = 1.7$ Hz, 1 H, H-5), AB sub-spectrum with $\delta_A = 6.48$ (H-6), $\delta_B = 6.46$ (H-7), $J_{AB} = 5.5$ Hz, the lines of the A part are split into doublets with $J = 1.7$ Hz; 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 $CH_3C_6H_4SO_2$).

^{13}C-NMR/DEPT (62.9 MHz, $CDCl_3$): δ= 21.6 (+, $CH_3C_6H_4SO_2$); 42.2 (-, CH_2-N); 81.9 (C_q, C-4); 85.05 (C_q, C-2); 87.9 (+, C-5); 93.3 (C_q, C-1); 127.0 (+, C-2/6 of the tosyl group); 130.0 (+, C-3/5 of the tosyl group); 134.4 (+, C-6); 135.7 (+, C-7); 136.7 (C_q, C-4 of the tosyl group); 144.1 (C_q, C-1 of the tosyl group); 183.9 (C_q, C-3).

IR ($CHCl_3$ film, cm^{-1}): 3395, 3280 (N-H); 3110 (=C-H); 1768 with shoulder at 1750 (C=O); 1600 (C=C); 1495 (NH); 1430, 1340 (SO_2); 1163 cm^{-1} (SO_2).

Elemental Analysis: Calculated for $C_{15}H_{13}Cl_4NO_4S$ (445.15): C, 40.47%; H, 2.94%; Cl, 31.86%; N: 3.15%; S, 7.20%. Found: C, 40.24%; H, 3.02%; Cl, 31.63%; N, 3.15%; S, 7.15%.

References and Notes

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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.