# 1,1-Dihalo-1-(methylsulfonyl)methanesulfonamides

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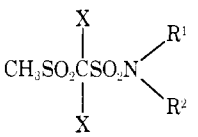
**The preparation of a series of 1,1-dihalo-1-(methylsulfonyl)methanesulfonamides *via* the base-induced halogenation of the corresponding 1-(methylsulfonyl)methanesulfonamides is described. Analytical and nmr spectral data for the compounds are presented.**

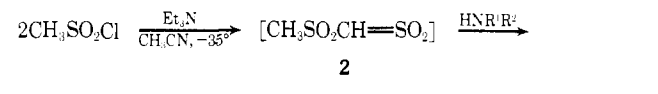
Although there are a number of reports in the literature concerning the halogenation of "active methylene" compounds (*1–4, 7*), only one brief report has appeared concerning compounds containing a methylene group bearing two sulfonyl functions (*5*). In this paper we would like to report the synthesis of a series of 1,1-dihalo-1-(methylsulfonyl)methanesulfonamides (**1**, Table I) *via* the halogenation of the corresponding 1-(methylsulfonyl)methanesulfonamides.



X = Br or Cl

**1**

The 1-(methylsulfonyl)methanesulfonamides (**3**, Tables II and III) were prepared by the method of Opitz et al. (*6*), which involves the reaction of "sulfene" dimer (**2**) with the appropriate amine (Equation 1). The 1,1-dihalo-



**2**

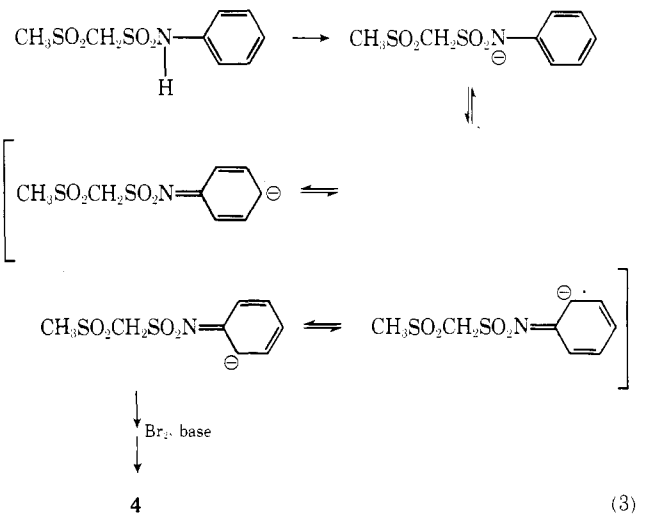
$$CH_3SO_2CH_2SO_2NR^1R^2 \quad (1)$$

**3**

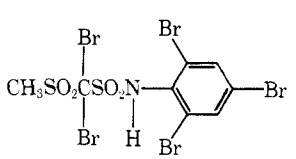
1-(methylsulfonyl)methanesulfonamides (**1**) were prepared by halogenation of the corresponding 1-(methylsulfonyl)methanesulfonamide (**3**) with sodium hypohalite in either water or water–dioxane mixtures (Equation 2).

$$3 \xrightarrow{NaOX} 1 \quad X = Br \text{ or } Cl \quad (2)$$

In the case of 1-(methylsulfonyl)methanesulfonanilide (**3**; $R^1$=H, $R^2$=$C_6H_5$) bromination of the aromatic ring occurred in addition to bromination of the active methylene group giving rise to the pentabromo compound (**4**). Apparently, the sulfonamide linkage is sufficiently acidic to permit the aromatic ring to brominate, in the presence of base, as readily as phenol (Equation 3).



**4** (3)



**4**

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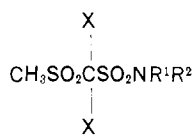
**Table I. 1,1-Dihalo-1-(methylsulfonyl)methanesulfonamides, 1**



| $R^1$ | $R^2$ | X | Mp, °C | Yield, % |
|---|---|---|---|---|
| H | H | Br | 232–233(d) | 67 |
| H | $CH_3$ | Br | 128–129.5 | 86 |
| H | n-$C_6H_{13}$ | Br | 71.5–73 | 53 |
| H | n-$C_{12}H_{25}$ | Br | 77–79 | 96 |
| H | $C_6H_2Br_3$ | Br | 202–203 | 49 |
| $CH_3$ | $CH_3$ | Br | 119–120 | 90 |
| $CH_2CH_2CH_2CH_2CH_2$ | | Cl | 91–93 | 54 |
| $CH_2CH_2OCH_2CH_2$ | | Br | 125–126 | 63 |
| $CH_2CH_2OCH_2CH_2$ | | Cl | 115–117 | 98 |
| $CH_3$ | $C_6H_5$ | Br | 150–151.5 | 53 |
| $C_6H_5$ | $C_6H_5$ | Br | 189–190 | 70 |

**Table II. 1-(Methylsulfonyl)methanesulfonamides, 3**

$CH_3SO_2CH_2SO_2NR^1R^2$

| $R^1$ | $R^2$ | Mp, °C | Yield, % |
|---|---|---|---|
| H | H | 160–161 | 67 |
| H | $CH_3$ | 110–111 | 55 |
| H | n-$C_6H_{13}$ | 131–132 | 60 |
| H | n-$C_{12}H_{25}$ | 138–139 | 65 |
| H | $C_6H_5$ | 154–156[a] | 70 |
| $CH_3$ | $CH_3$ | 112–114[b] | 78 |
| $CH_2CH_2CH_2CH_2CH_2$ | | 200–202 | 74 |
| $CH_2CH_2OCH_2CH_2$ | | 221–222 | 66 |
| $CH_3$ | $C_6H_5$ | 131–132 | 70 |
| $C_6H_5$ | $C_6H_5$ | 172–173 | 73 |

[a] Literature (*6*), mp 155–156°. [b] Literature (*6*), mp 113–114°.

## Experimental

***1,1-Dibromo-1-(methylsulfonyl)methanesulfonamides.*** To a solution of 4.0 grams (0.10 mol) of sodium hydroxide in 150 ml of water was added 0.05 mol of the 1-(methylsulfonyl)methanesulfonamide. The solution was cooled to 5°, and 16.0 grams (0.10 mol) of bromine were added dropwise with stirring over a 15-min period. After stirring for an additional 15 min, the product was filtered off and recrystallized from methanol or ethanol to give the pure 1,1-dibromo-1-(methylsulfonyl)methanesulfonamide as a white, crystalline solid (Tables I and IV).

***1,1-Dichloro-1-(methylsulfonyl)methanesulfonamides.*** To a solution of 4.0 grams of the 1-(methylsulfonyl)-methanesulfonamide in 200 ml of dioxane were added 100 ml of 5% sodium hypochlorite solution. The reaction mixture was allowed to stir for 1 hr at room temperature. The reaction mixture was acidified with dilute hydrochloric acid, and the water/dioxane removed in vacuo leaving

**Table III. Analytical and NMR Data for 1-(Methylsulfonyl)methanesulfonamides, 3**

$CH_3SO_2CH_2SO_2NR^1R^2$

| | | Analyses | | | | | | | | NMR data[a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd | | | | Found | | | | | | | |
| $R^1$ | $R^2$ | C | H | N | S | C | H | N | S | Solvent | $CH_3$-$SO_2$ | $SO_2$-$CH_2$-$SO_2$ | Other protons |
| H | H | 13.87 | 4.07 | 8.09 | 37.02 | 14.21 | 4.05 | 8.41 | 37.22 | DMSO-$d_6$ | 3.20 | 4.98 | 7.35(s, $NH_2$) |
| H | $CH_3$ | 19.24 | 4.85 | 7.48 | 34.25 | 19.45 | 4.60 | 7.62 | 33.55 | DMSO-$d_6$ | 3.18 | 5.06 | 2.62(d, $NCH_3$); 7.20–7.60 (brd q, NH) |
| H | *n*-$C_6H_{13}$ | 37.33 | 7.44 | 5.44 | 24.92 | 37.51 | 7.53 | 5.79 | 25.19 | $CDCl_3$ | | 4.60 | 0.80–1.90 (m, $(CH_2)_4CH_3$); 3.00–3.50 (m, $CH_3SO_2$, and $NCH_2$); 5.70–6.10 (s, NH) |
| H | *n*-$C_{12}H_{25}$ | 49.24 | 9.15 | 4.10 | 18.78 | 49.26 | 9.18 | 4.11 | 18.82 | 1:1 DMSO/acetone-$d_6$ | 3.20 | 5.00 | 0.85 (t, $CH_3$); 1.35 (brd s, —$(CH_2)_{10}$—); 7.00–8.00 (brd s, NH) |
| H | $C_6H_5$ | | | | | | | | | Acetone-$d_6$ | 3.30 | 4.85 | 7.20–7.65 (brd m, NH, $C_6H_5$) |
| $CH_3$ | $CH_3$ | | | | | | | | | Acetone-$d_6$ | 3.20 | 4.83 | 2.95 (s, $N(CH_3)_2$) |
| $CH_2CH_2CH_2CH_2CH_2$ | | 34.84 | 6.26 | 5.80 | 26.57 | 34.83 | 6.41 | 5.91 | 26.69 | ... | ... | ... | ... |
| $CH_2CH_2OCH_2CH_2$ | | 29.62 | 5.38 | 5.76 | 26.36 | 30.26 | 5.41 | 5.99 | 26.35 | DMSO-$d_6$ | 3.65 | 5.23 | 3.18–3.30 (brd s,  |
| $CH_3$ | $C_6H_5$ | 41.05 | 4.98 | 5.32 | 24.35 | 41.24 | 4.95 | 5.51 | 24.37 | $CDCl_3$ | 3.50 | 4.45 | 3.25 (s, $NCH_3$); 7.50 (s, $C_6H_5$) |
| $C_6H_5$ | $C_6H_5$ | 51.67 | 4.65 | 4.30 | 19.71 | 51.99 | 4.71 | 4.59 | 19.82 | DMSO-$d_6$ | 3.25 | 5.55 | 7.20–7.90 (m, arom) |

[a] The NMR data are given in ppm ($\delta$) downfield from TMS. The spectra were recorded on a Varian T-60 spectrometer with TMS as an internal standard.

**Table IV. Analytical and NMR Data for 1,1-Dihalo-1-(methylsulfonyl)methanesulfonamides, 1**

$CH_3SO_2CX_2SO_2NR^1R^2$

| | | | Analyses | | | | | | | | | | NMR data[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd | | | | | Found | | | | | | | |
| $R^1$ | $R^2$ | X | C | H | Br(Cl) | N | S | C | H | Br(Cl) | N | S | Solvent | $CH_3$-$SO_2$ | Other protons |
| H | H | Br | 7.26 | 1.52 | 48.28 | 4.23 | 19.37 | 7.65 | 1.52 | 48.70 | 4.58 | 19.81 | Acetone-$d_6$ | 3.60 | 7.45 (s, $NH_2$) |
| H | $CH_3$ | Br | 10.44 | 2.04 | 46.32 | 4.06 | 18.59 | 11.03 | 1.96 | 47.00 | 4.34 | 18.60 | DMSO-$d_6$ | 3.33 | 2.90 (d, $NCH_3$); 8.6–8.9 (brd q, NH) |
| H | *n*-$C_6H_{13}$ | Br | 23.14 | 4.13 | 38.49 | 3.37 | 15.45 | 23.32 | 4.00 | 38.20 | 3.63 | 16.12 | $CDCl_3$ | 3.60 | 0.65–1.20 (brd m, hexyl $CH_3$); 1.20–2.10 (brd s, $(CH_2)_4$); 5.10–5.50 (brd t, NH); 3.60 (t, $NCH_2$—) |
| H | *n*-$C_{12}H_{25}$ | Br | 33.68 | 5.85 | 32.00 | 2.81 | 12.84 | 34.13 | 5.89 | 31.80 | 3.04 | 13.16 | $CDCl_3$ | 3.58 | 0.85 (t, $CH_3$); 1.25 (brd s, $(CH_2)_{10}$), 3.45 (t, $NCH_2$—); 5.23 (t, NH) |
| H | $C_6H_2Br_3$ | Br | 14.93 | 0.94 | 62.06 | 2.17 | 9.96 | 15.22 | 1.04 | 61.60 | 2.35 | 10.00 | Acetone-$d_6$ | 3.60 | 8.00 (s, arom); 8.40–9.00 (brd s, NH) |
| $CH_3$ | $CH_3$ | Br | 13.38 | 2.53 | 44.51 | 3.90 | 17.86 | 13.81 | 2.55 | 45.00 | 4.05 | 17.97 | $CDCl_3$ | 3.52 | 3.20 (s, $N(CH_3)_2$) |
| $CH_2CH_2CH_2CH_2CH_2$ | | Cl | 27.10 | 4.22 | 22.86 | 4.51 | 20.67 | 26.80 | 4.05 | 22.70 | 4.46 | 20.50 | ... | ... | ... |
| $CH_2CH_2OCH_2CH_2$ | | Br | 17.97 | 2.76 | 39.84 | 3.49 | 15.99 | 18.18 | 2.69 | 40.00 | 3.67 | 16.03 | DMSO-$d_6$ | | 3.70 (brd s) |
| $CH_2CH_2OCH_2CH_2$ | | Cl | 23.08 | 3.55 | 22.71 | 4.49 | 20.54 | 23.00 | 3.51 | 22.80 | 4.55 | 20.60 | DMSO-$d_6$ | 3.60 | 3.65 (brd s,  |
| $CH_3$ | $C_6H_5$ | Br | 25.67 | 2.63 | 37.95 | 3.32 | 15.23 | 25.63 | 2.49 | ... | 3.39 | 14.89 | DMSO-$d_6$ | 3.60 | 3.60 (s, $NCH_3$), 7.30–7.90 (m, arom) |
| $C_6H_5$ | $C_6H_5$ | Br | 34.80 | 2.71 | 33.07 | 2.90 | 13.27 | 34.91 | 2.56 | 32.50 | 3.00 | 13.23 | DMSO-$d_6$ | 3.50 | 7.00–8.30 (m, arom) |

[a] The NMR data are given in ppm ($\delta$) downfield from TMS. The spectra were recorded on a Varian T-60 spectrometer with TMS as an internal standard.

a white solid. The solid was slurried with water, filtered, air dried, and recrystallized from absolute ethanol to give the pure 1,1-dichloro-1-(methylsulfonyl)methanesulfonamide (Tables I and IV).

### Literature Cited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