

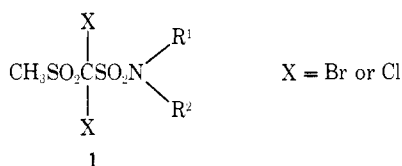
1,1-Dihalo-1-(methylsulfonyl)methanesulfonamides

Christian T. Goralski¹ and Thomas C. Klingler

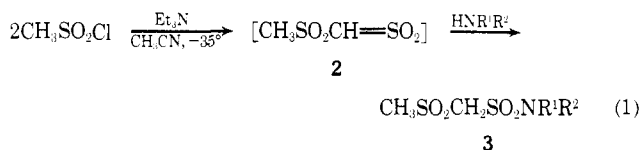
Halogens Research Laboratory, Dow Chemical Co., Midland, Mich. 48640

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.

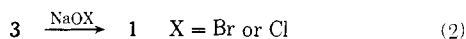
Although there are a number of reports in the literature concerning the halogenation of "active methylene" compounds (1-4, 7), only one brief report has appeared concerning compounds containing a methylene group bearing two sulfonyl functions (5). In this paper we would like to report the synthesis of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



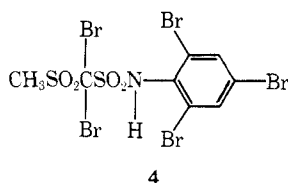
The 1-(methylsulfonyl)methanesulfonamides (3, Tables II and III) were prepared by the method of Opitz et al. (6), which involves the reaction of "sulfene" dimer (2) with the appropriate amine (Equation 1). The 1,1-dihalo-



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).



In the case of 1-(methylsulfonyl)methanesulfonanilide (3; R¹=H, R²=C₆H₅) 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).

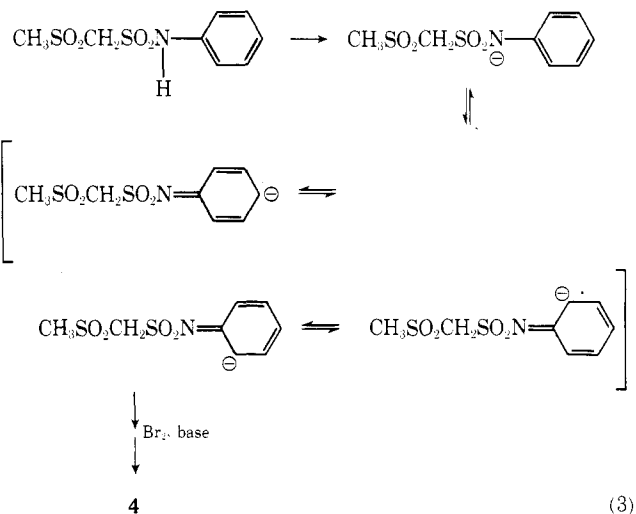


Table I. 1,1-Dihalo-1-(methylsulfonyl)methanesulfonamides, 1

$\begin{array}{c} \text{X} \\ \\ \text{CH}_3\text{SO}_2\text{C} \text{---} \text{SO}_2\text{NR}^1\text{R}^2 \\ \\ \text{X} \end{array}$				
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 ₆ H ₁₃	Br	71.5-73	53
H	n-C ₁₂ H ₂₅	Br	77-79	96
H	C ₆ H ₂ Br ₃	Br	202-203	49
CH ₃	CH ₃	Br	119-120	90
	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	Cl	91-93	54
	CH ₂ CH ₂ OCH ₂ CH ₂	Br	125-126	63
	CH ₂ CH ₂ OCH ₂ CH ₂	Cl	115-117	98
CH ₃	C ₆ H ₅	Br	150-151.5	53
C ₆ H ₅	C ₆ H ₅	Br	189-190	70

Table II. 1-(Methylsulfonyl)methanesulfonamides, 3

$\text{CH}_3\text{SO}_2\text{CH}_2\text{SO}_2\text{NR}^1\text{R}^2$			
R ¹	R ²	Mp, °C	Yield, %
H	H	160-161	67
H	CH ₃	110-111	55
H	n-C ₆ H ₁₃	131-132	60
H	n-C ₁₂ H ₂₅	138-139	65
H	C ₆ H ₅	154-156 ^a	70
CH ₃	CH ₃	112-114 ^b	78
	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	200-202	74
	CH ₂ CH ₂ OCH ₂ CH ₂	221-222	66
CH ₃	C ₆ H ₅	131-132	70
C ₆ H ₅	C ₆ H ₅	172-173	73

^a Literature (6), mp 155-156°. ^b Literature (6), mp 113-114°.

¹ To whom correspondence should be addressed.

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 ₃ SO ₂ CH ₂ SO ₂ NR ¹ R ²													
Analyses										NMR data ^a			
R ¹	R ²	Calcd				Found				Solvent	CH ₃ -SO ₂	SO ₂ -CH ₂ -SO ₂	Other protons
		C	H	N	S	C	H	N	S				
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	<i>n</i> -C ₆ H 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) ₄ CH ₃); 3.00–3.50 (m, CH ₃ SO ₂ , and NCH ₃); 5.70–6.10 (s, NH)
H	<i>n</i> -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 ₆ H ₅									Acetone-d ₆	3.30	4.85	7.20–7.65 (brd m, NH, C ₆ H ₅)
CH ₃	CH ₃									Acetone-d ₆	3.20	4.83	2.95 (s, N(CH ₃) ₂)
CH ₂ CH ₂ CH ₂ CH ₂ CH ₂		34.84	6.26	5.80	26.57	34.83	6.41	5.91	26.69	...	...	...	...
CH ₂ CH ₂ OCH ₂ CH 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, N )
CH ₃	C ₆ H 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 ₆ H ₅)
C ₆ H ₅	C ₆ H 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 (δ) 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 ₃ SO ₂ CX ₂ SO ₂ NR ¹ R ²															
R ¹	R ²	X	Analyses										NMR data ^a		
			Calcd					Found					Solvent	CH ₃ -SO ₂	Other protons
			C	H	Br(Cl)	N	S	C	H	Br(Cl)	N	S			
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 ₆ H 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 ₆ H ₂ Br 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 ₂ CH ₂ CH ₂ CH ₂ CH ₂		Cl	27.10	4.22	22.86	4.51	20.67	26.80	4.05	22.70	4.46	20.50	...	...	...
CH ₂ CH ₂ OCH ₂ CH 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 ₂ CH ₂ OCH ₂ CH 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, N )
CH ₃	C ₆ H 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 ₆ H ₅	C ₆ H 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 (δ) 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

- (1) Baker, D. R., Williamson, T. B. (to Stauffer Chemical Co.), U.S. Patent 3,142,616 (July 28, 1964).
- (2) Carpino, L. A., *J. Amer. Chem. Soc.*, **80**, 599 (1958).
- (3) Freeman, F., *Chem. Rev.*, **69**, 591 (1969).
- (4) Gum, Jr., W. F., Goralski, C. T. (to Dow Chemical Co.), U.S. Patent 3,703,515 (Nov. 21, 1972).
- (5) Kohler, E. P., Tishler, M., *J. Amer. Chem. Soc.*, **57**, 217 (1935).
- (6) Opitz, G., Kleeman, M., Bucher, D., Walz, G., Rieth, K., *Angew. Chem., Int. Ed.*, **5**, 595 (1966).
- (7) Truce, W. E., Klingler, T. C., Parr, J. E., Feuer, H., Wu, D. K., *J. Org. Chem.*, **34**, 3104 (1969).

Received for review October 1, 1973. Accepted February 4, 1974.