Preparation of Trichloromethanesulfonamides via Trichloromethanesulfenamides

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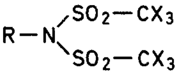
Nucleophilic substitution reactions of *N*-alkyl bis[trifluoromethane]sulfonimides **1a** have recently been reported[1].

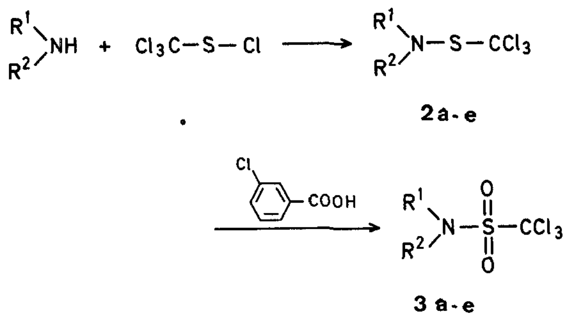


$R-N(SO_2-CX_3)_2$

1a X = F
b X = Cl

Similar reactions are anticipated for the corresponding compounds with chlorine in place of fluorine. The trichloro compounds **1b** have two potential advantages over the corresponding trifluoro compounds. The trichloro compounds would be far less expensive and may also be less prone to attack at sulfur because of greater steric shielding by the larger trichloromethyl group. However, preparation of these compounds from trichloromethanesulfonamides presented a problem. Only one example of the latter compounds has previously been prepared[2]. The difficulty in synthesizing these compounds is that the inexpensive and readily available trichloromethanesulfonyl chloride[3] does not react with amines to produce trichloromethanesulfonamides[2,4]. The only trichloromethanesulfonamide recorded was produced by oxidation of the trichloromethanesulfenamide of *p*-chloroaniline **2a** with potassium permanganate[2]. This afforded the corresponding sulfonamide **3a** albeit in only 36% yield. However, treatment of trichloromethanesulfenamides derived from aliphatic amines with potassium permanganate failed to produce the corresponding sulfonamides in our hands. This paper reports our finding that trichloromethanesulfenamides **2** derived from aliphatic amines can be oxidized with *m*-chloroperoxybenzoic acid in good yields to the corresponding sulfonamides **3**. This sequence is outlined in Scheme **A**.

Reaction of trichloromethanesulfenyl chloride with two molar equivalents of amine gave the corresponding trichloromethanesulfenamide **2** in good yields as shown in Table 1. The I.R. and ^{1}H-N.M.R. spectra of these compounds support the assigned structures. Since these materials decompose on standing overnight at room temperature, they were oxidized with *m*-chloroperoxybenzoic acid to the corresponding sulfonamides **3** soon after their preparation. The yields in this oxidation and the properties of these sulfona-



	R^1	R^2
a	4-Cl—C_6H_4	H
b	n-C_6H_{13}	H
c	sec-C_4H_9	H
d	t-C_4H_9	H
e	i-C_3H_7	i-C_3H_7

Scheme A

mides are recorded in Table 2. The I.R., ^{1}H-N.M.R. and mass spectra of sulfonamides **3** support their assigned structures. In addition, satisfactory microanalyses were obtained for the new sulfonamides (**3b–f**).

An attempt to prepare sulfonimide **1b** (R = n-C_6H_{13}) from the sulfenamide-sulfonamide **4a** was unsuccessful.

4a R^1 = n-C_6H_{13}, R^2 = CCl_3
b R^1 = cyclo-C_6H_{11}, R^2 = C_6H_5
c R^1 = cyclo-$C_{12}H_{23}$, R^2 = C_6H_5

Treatment of **4a** with m-chloroperoxybenzoic acid or trifluoroperoxyacetic acid failed to give **1b** (R = n-C_6H_{13}). However, sulfenamide-sulfonamides **4b** and **4c** could be oxidized to the corresponding di-(benzene)-sulfonimides with m-chloroperoxybenzoic acid in hexane at reflux in 65 and 84% yield, respectively. Sulfenamide-sulfonamides **4b** and **4c** were obtained in 82 and 34% yield respectively by converting the corresponding sulfonamides to their lithium salts with n-butyllithium and treating these salts with benzenesulfenyl chloride.

Table 1. Yield and Physical Properties of Trichloromethanesulfenamides **2**.

Compound	Yield [%]	b.p./torr	^{1}H-N.M.R. (CCl_4): δ [ppm]
2b	88	88°/0.50	0.69–1.88 (m, 11H); 3.33 (m, 2H)
2c	89	59°/0.80	0.76–2.04 (m, 8H); 3.47 (m, 1H)
2d	86	45°/0.08	1.31 (s, 9H); 3.88 (br, 1H)
2e	72	67°/0.10	1.29 (d, 6H, J = 7 Hz); 3.64 (m, 1H, J = 7 Hz)

N-n-Hexyltrichloromethanesulfenamide (2b):

A solution of distilled trichloromethanesulfenyl chloride (0.93 g, 5.0 mmol) in cyclohexane (25 ml) is added over 45 min, to a solution of n-hexylamine (1.02 g, 10.0 mmol) in cyclohexane (50 ml) cooled in an ice/water bath. After 15 h, the mixture is filtered, the precipitate is washed with cyclohexane, and the washings and filtrate combined. The solvent is removed using a rotary evaporator and the resulting liquid distilled under vacuum to give sulfenamide **2b**; yield: 1.10 g (88%); b.p. 88°/0.50 torr.

The other trichloromethanesulfenamides were prepared similarly.

N-n-Hexyltrichloromethanesulfonamide (3b):

To a solution of N-n-hexyltrichloromethanesulfenamide (3.46 g, 13.5 mmol) dissolved in hexane (100 ml) is added m-chloroperoxybenzoic acid (85%, 6.10 g, 30 mmol). The mixture is stirred and heated under reflux for 12 h. At the end of this time the mixture is cooled, filtered, and the filtrate evaporated. The residue is chromatographed on a silica gel column (32 g, 1 × 35 cm) using benzene as eluent. The solid sulfonamide **3b** so obtained is recrystallized from hexane; yield: 3.19 g (82%); m.p. 34–35°.

$C_7H_{14}Cl_3NO_2S$	calc.	C 29.75	H 4.99	S 11.34
(282.6)	found	29.79	5.00	11.38

The other trichloromethanesulfonamides were prepared similarly.

N-Cyclohexyl-N-(benzenesulfenyl)-benzenesulfonamide (4b):

To a solution of N-cyclohexylbenzenesulfonamide (0.24 g, 1.02 mmol) dissolved in anhydrous tetrahydrofuran (5 ml), cooled in a Dry Ice/acetone bath, is added 1.6 molar n-butyllithium solution in hexane (0.63 ml, 1.0 mmol) dropwise over 0.5 h. The solution is warmed to 0° and benzenesulfenyl chloride (0.15 g, 1.05 mmol) dissolved in anhydrous tetrahydrofuran (1 ml) is added dropwise over 0.75 h. After being stirred for 15 h at room temperature, the mixture is poured into water (100 ml) and extracted with diethyl ether (3 × 20 ml). The ethereal extracts are washed sequentially with water (2 × 15 ml) and brine (2 × 15 ml) and dried over anhydrous magnesium sulfate. The mixture is filtered and the filtrate evaporated to a yellow oil which is chromatographed on silica gel (32 g, 1 × 35 cm). Elution with chloroform gives N-cyclohexyl-N-(benzenesulfenyl)-benzenesulfonamide (**4b**) as white crystals, which are recrystallized from 95% ethanol; yield: 0.29 g (82%); m.p. 118.5–119.0°.

$C_{18}H_{21}NO_2S_2$	calc.	C 62.22	H 6.10	S 18.45
(347.5)	found	62.20	5.99	18.35

I.R. (CCl_4): ν_{max} = 1355; 1165 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 0.78–1.87 (m, 10H); 4.06 (m, 1H); 7.00–8.03 ppm (m, 10H).

Compound **4c** was prepared similarly; m.p. 166.5–167°

$C_{24}H_{29}NO_2S_2$	calc.	C 66.78	H 7.71	S 14.86
(427.6)	found	66.50	7.87	14.77

Table 2. Yield and Physical Properties of Trichloromethanesulfonamides **3**.

Compound	Yield [%]	m.p.	Molecular formula[a]	I.R. (CCl_4): ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4): δ [ppm]
3b	94	34–35° (hexane)	$C_7H_{14}Cl_3NO_2S$ (282.6)	3790; 3520; 1380; 1195	0.62–1.90 (m, 11H); 3.39 (m, 2H); 5.62 (t, 1H, J = 6 Hz)
3c	80	83.5–84.5° (hexane)	$C_5H_{10}Cl_3NO_2S$ (254.6)	3300; 3100; 1370; 1190	0.82–2.80 (m, 8H); 3.66 (m, 1H); 5.55 (d, 1H, J = 9 Hz)
3d	57	92–94° (methanol)	$C_5H_{10}Cl_3NO_2S$ (254.6)	3360; 3270; 1350; 1180	1.48 (s, 9H); 5.41 (br, 1H)
3e	68	96.5–97.5° (hexane)	$C_7H_{14}Cl_3NO_2S$ (282.6)	1380; 1265	1.40 (d, 6H, J = 7 Hz); 4.05 (m, 1H, J = 7 Hz)

[a] All products gave satisfactory microanalyses (C ±0.06%, H ±0.09%, Cl ±0.07%).

I.R. (CHCl$_3$): ν_{max} = 1330; 1130 cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$): δ = 1.28 (s, 22 H); 4.27 (s, 1 H); 7.12–8.02 ppm (m, 10 H).

N-Cyclohexyl-N,N-di-(benzene)-sulfonimide:

N-Cyclohexyl-*N*-(benzenesulfenyl)-benzenesulfonamide (0.21 g, 0.62 mmol) is dissolved in hexane (5 ml) and *m*-chloroperoxybenzoic acid (85%, 0.28 g, 1.49 mmol) is added. The mixture is stirred and heated under reflux for 5 h, then cooled and the solvent removed by rotary evaporation. The residue is dissolved in chloroform and chromatographed on a column of silica gel (32 g, 1 × 35 cm). Elution with chloroform gives *N*-cyclohexyl-*N*,*N*-di-(benzene)-sulfonimide as white crystals; yield: 0.15 g (65%). The spectra of this compound were identical with an authentic sample prepared according to the method of Baumgarten et al.[5] *N*-Cyclododecyl-*N*,*N*-di-(benzene)-sulfonimide was prepared similarly.

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