

Base-induced Conversion of Dichloromethanesulfonyl Chloride to Trichloromethanesulfinate

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Dichloromethanesulfonyl chloride (*1*) is converted to trichloromethanesulfinate (*3*) when treated with triethylamine or pyridine. The reaction is suggested to proceed *via* an intermediate sulfene *2*.

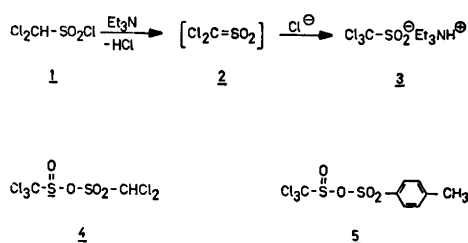
When trichloromethanesulfinate (*3*) is treated with triethylammonium bromide a halogen exchange is observed, as shown by a mass spectrometric investigation. This exchange reaction may also proceed *via* dichlorosulfene (*2*).

Mass spectra of trichloromethanesulfonyl chloride and trichloromethanesulfonyl bromide are discussed.

The conversion of sulfonyl chlorides to halosulfonates have not previously been observed. Intermediate halosulfonates have, however, been postulated¹ in the formation of sulfines from sulfonyl chlorides when treated with a base. This paper describes the reaction of dichloromethanesulfonyl chloride (*1*) when treated with triethylamine or pyridine. This reaction is shown to yield trichloromethanesulfinate (*3*).

Dichloromethanesulfonyl chloride (*1*) was treated with an equivalent amount of triethylamine or pyridine in ethyl ether or benzene at room temperature to yield a product which separated during the reaction. This product was shown to be trichloromethanesulfinate (*3*), and was characterized by transforming it into the trichloromethanesulfinyl chloride² or into the crystalline morpholide.³ The crystalline trichloromethanesulfonyl chloride⁴ and the corresponding bromide⁵ were also prepared by oxidation with chlorine or bromine in water.

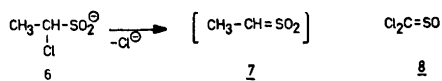
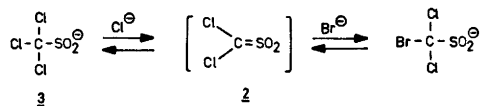
Chloromethanesulfonyl chloride is not converted to dichloromethanesulfinate when treated with triethylamine. This was shown by the fact that the corresponding dichloromethanesulfonyl



chloride could not be detected in the reaction mixture after oxidation with chlorine in water. Consequently, the reaction of dichloromethanesulfonyl chloride seems to be a special case due to the effect of the two halogen atoms of the dichloromethyl grouping.

The conversion of dichloromethanesulfonyl chloride (*1*) to trichloromethanesulfinate (*3*) may proceed *via* an intermediate sulfene *2*⁶ which, when attacked by a chloride ion, yields the sulfinate *3*. A second mechanism for the reaction should also be considered. This mechanism involves an intermediate sulfinyl sulfonate *4*, formed in a reaction of the intermediate sulfene *2* and dichloromethanesulfonyl chloride (*1*).⁷ The sulfinylsulfonate *4* then decomposes in the presence of a base to the sulfinate *3* and the sulfene *2*. The sulfene *2* can react further in a chain reaction. Intermediate sulfinyl sulfonates, *e.g.* *5*, which lack α -protons, should not react further. However, in the presence of toluenesulfonyl chloride the conversion of dichloromethanesulfonyl chloride proceeds in the normal way, and the toluenesulfonyl chloride is recovered quantitatively. This experiment shows that a sulfinyl sulfonate does not seem to be an intermediate in the reaction.

It is of interest to note that there is a halogen exchange in trichloromethanesulfinate (3) when this compound is treated with triethylammonium bromide. This halogen exchange was demonstrated by a mass spectrometric investigation (see experimental), and may proceed *via* dichlorosulfene (2), which is in rapid equilibrium with trichloromethanesulfinate (3).



The formation of dichlorosulfene (2) from trichloromethanesulfinate (3) is analogous to the decomposition of 1-chloroethanesulfinate (6) to yield the intermediate methylsulfene (7).⁸ Dichlorosulfene (8) has recently been prepared,^{9,10} and was found to be a rather stable compound. It is therefore reasonable to predict that dichlorosulfene (2) is also stable. It is of interest to note that theoretical calculations predict that electron-donating substituents stabilize sulfenes.¹¹

The Fourier transform ¹³C NMR spectrum of the triethylammonium salt of trichloromethanesulfonic acid in a chloroform solution exhibits a signal at 115.6 ppm (downfield from TMS; benzene external standard $\delta_{(\text{benzene})}$ 127.6 ppm) due to the carbon atom of the trichloromethyl group. This chemical shift is comparable with those of trichloromethanesulfonyl chloride (109.6 ppm) and trichloromethanesulfonyl chloride (106.8 ppm). The *sp*²-hybridized carbon of dichlorosulfene (2) is expected to exhibit a chemical shift further downfield. If there is a rapid equilibrium between dichlorosulfene (2) and trichloromethanesulfinate (3), there seems to be very little contribution from the carbon species of dichlorosulfene and the equilibrium must be strongly shifted towards the sulfinate 3.

It is known¹² that 2-chlorothiirane 1,1-dioxide is formed, when chloromethanesulfonyl chloride is treated with triethylamine in the presence of diazomethane, thus trapping the intermediate

sulfene. However, when the base-induced conversion of dichloromethanesulfonyl chloride (1) was carried out in the presence of diazomethane no reaction with the suggested intermediate dichlorosulfene (2) and diazomethane could be observed.

Trichloromethanesulfonyl chloride and the corresponding bromide have been used for the halogenation of hydrocarbons.⁵ The Cl₃C-SO₂· radical has been suggested as being the hydrogen abstractor in the halogenation reaction with trichloromethanesulfonyl chloride, whereas in the reaction with the corresponding bromide, the Cl₃C· radical is suggested as being the hydrogen abstractor.⁵

This difference between the sulfonyl chloride and the corresponding bromide is also reflected in the mass spectrometric fragmentation pattern of the two compounds. No molecular ion peaks are observed in the spectra. The mass spectrum of the sulfonyl chloride exhibits peaks at *m/e* 181 and 117 due to the (Cl₃C-SO₂)⁺ and (Cl₃C)⁺, respectively. A peak at *m/e* 298 must be an artefact due to radical dimerization to the bis(trichloromethyl) sulphone. The mass spectrum of the sulfonyl bromide, on the other hand, did not exhibit any trichloromethanesulfonyl fragment, (Cl₃C-SO₂)⁺, at *m/e* 181. The parent peak was the trichloromethyl radical ion, (Cl₃C)⁺, at *m/e* 117.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were measured on a Perkin Elmer Model 421 infrared spectrophotometer. ¹H NMR spectra (TMS internal standard) were recorded on a Varian Model A-60 A instrument. ¹³C NMR spectra were recorded on a Varian HA-100-D spectrometer. Mass spectra were obtained when using an LKB Model 9000 mass spectrometer (direct inlet).

Pyridinium and triethylammonium salts of trichloromethanesulfonic acid. A solution of pyridine (7.9 g, 0.1 mol) or triethylamine (10.1 g, 0.1 mol) in ethyl ether (25 ml) was added during 15 min to dichloromethanesulfonyl chloride¹³ (18.3 g, 0.1 mol) in ethyl ether (100 ml). The mixture was stirred for 1 h at room temperature. The pyridinium salt thus formed was filtered off, washed with ethyl ether and dried *in vacuo*. Yield: 25 g (95 %); m.p. 115–117 °C. IR (CHCl₃) 1200 cm⁻¹ (S=O); ¹H NMR (CHCl₃) δ 10.4–9.2 ppm (m, pyridinium protons).

The triethylammonium salt, prepared as described above for the pyridinium salt, was a

heavy oil. This oil was separated from the ether phase, and traces of ethyl ether dissolved in the oil were removed *in vacuo*. Yield: 27 g (95 %); IR (film) 1220 cm^{-1} (S=O); ^1H NMR (CHCl_3) δ 1.2 (t, 9, CH_3) and 2.8–3.2 ppm (two overlapping quartets, 6, CH_2 , coupling with the CH_3 and N–H).

Trichloromethanesulfonyl chloride. Thionyl chloride (23.8 g, 0.2 mol) was added to the pyridinium salt of trichloromethanesulfinic acid (26.2 g, 0.1 mol) or its triethylammonium salt (28.4 g, 0.1 mol) in benzene (100 ml). The mixture was heated under reflux for 30 min and then cooled to room temperature. Insoluble salts were removed by filtration, and the solution evaporated *in vacuo*. The residue was distilled under reduced pressure to give trichloromethanesulfonyl chloride. Yield: from the pyridinium salt, 14 g (69 %), and from the triethylammonium salt, 13 g (64 %); b.p. 53–54 $^\circ\text{C}/9$ mmHg (lit.² b.p. 36–38 $^\circ\text{C}/1$ mmHg); m.p. 18 $^\circ\text{C}$; n_D^{25} 1.5455; IR (film) 1200 cm^{-1} (lit.² 1190 cm^{-1} , S=O).

The trichloromethanesulfonyl chloride was further characterized as the corresponding morpholide: m.p. 88–89 $^\circ\text{C}$ (lit.³ m.p. 85–87 $^\circ\text{C}$). (Found: C 24.20; H 3.30; Cl 41.86; N 5.38; S 12.50. Calc. for $\text{C}_5\text{H}_8\text{Cl}_3\text{NO}_2\text{S}$: C 23.78; H 3.19; Cl 42.11; N 5.54; S 12.69).

Trichloromethanesulfonyl bromide. Triethylamine (10.1 g, 0.1 mol) was added to dichloromethanesulfonyl chloride (18.3 g, 0.1 mol) in benzene (100 ml), and the mixture was stirred at room temperature for 30 min. A solution of bromine (19.2 g, 0.12 mol) in water (200 ml) and benzene (100 ml) was then added in one portion to the trichloromethanesulfinate under vigorous stirring. The organic layer was allowed to separate after 15 min, washed with aqueous sodium bisulfite solution (10 %) to remove excess bromine, and then with water. The benzene solution was dried and evaporated *in vacuo* to give a crystalline residue. The crystals were dissolved in a minimum amount of ethanol. The product (trichloromethanesulfonyl bromide) was precipitated with water, filtered and dried *in vacuo*. Yield: 14.5 g (55 %); m.p. 138–140 $^\circ\text{C}$ (lit.⁵ m.p. 138–139 $^\circ\text{C}$); IR (CCl_4) 1400 and 1180 cm^{-1} (lit.⁵ 1398 and 1177 cm^{-1} , $-\text{SO}_2\text{Br}$); mass spectrum (20 eV, direct inlet) *m/e* (rel. intensity) CCl_3^+ 117 (100), 119 (94.5) and 121 (27.9).

Trichloromethanesulfonyl chloride. The pyridinium salt (5.2 g, 0.02 mol) or the triethylammonium salt (28.4 g, 0.1 mol) of trichloromethanesulfinic acid, was added to a water solution which was continuously saturated with chlorine. The reaction was stopped when no more chlorine was consumed. The product, trichloromethanesulfonyl chloride, which separated as white crystals during the oxidation, was filtered off and washed with water. For further purification, the crystals were dissolved in a minimum amount of ethanol and precipitated with water, then filtered and dried *in vacuo*. Yield: from the pyridinium salt, 3 g (68 %), and from the tri-

ethylammonium salt, 14 g (64 %); m.p. 140–141 $^\circ\text{C}$ (lit.⁴ 140–140.5 $^\circ\text{C}$); mass spectrum (20 eV, direct inlet) *m/e* (rel. intensity) CCl_3^+ 117 (100), 119 (95.11), 121 (32.1); 149 (0.26), 151 (0.27), 153 (0.09); $\text{Cl}_2\text{C}-\text{SO}_2^+$ 181 (1.58), 183 (1.53), 185 (0.53); $\text{Cl}_3\text{C}-\text{SO}_2-\text{CCl}_3^+$ 263 (0.24), 265 (0.40), 267 (0.27), 269 (0.10); $\text{Cl}_2\text{C}-\text{SO}_2-\text{CCl}_3^+$ 298 (0.074), 300 (0.14), 302 (0.12), 304 (0.05).

Treatment of dichloromethanesulfonyl chloride with diazomethane in the presence of triethylamine. Dichloromethanesulfonyl chloride (16.5 g, 0.09 mol) in ethyl ether (100 ml) and triethylamine (9.1 g, 0.09 mol) in ethyl ether (100 ml) were simultaneously added dropwise, to a stirred and cold solution (-40 to 50 $^\circ\text{C}$) of diazomethane¹⁴ (0.09 mol) in ethyl ether (200 ml). The addition requires about 30 min. The reaction mixture was stirred for an additional 30 min. Diazomethane was not consumed, as shown by its characteristic colour. Acetic acid was added dropwise in order to react with the diazomethane. The ether solution was separated from an insoluble residue. The residue (18 g) was oxidized with chlorine in water to give trichloromethanesulfonyl chloride. The sulfonyl chloride was dissolved in a minimum amount of ethanol, and then precipitated with water, filtered off and dried *in vacuo*. Yield 9 g, m.p. 140–141 $^\circ\text{C}$. The ether solution was washed with water and dried. Evaporation *in vacuo* gave a liquid residue (5 g).

Infrared spectrum (film) of this residue did not exhibit absorption typical of a sulfone (1300–1320 and 1140–1170 cm^{-1}). Distillation of the oily residue at reduced pressure gave a compound which was characterized as methyltrichloromethanesulfinate. B.p. 74–75 $^\circ\text{C}/9$ mmHg (lit.² b.p. 38–40 $^\circ\text{C}/1$ mmHg); n_D^{25} 1.5022; IR (film) 1190, 970, 795 and 820 cm^{-1} (lit.² IR 1190, S=O; 970, S–O–C; 795 and 822 cm^{-1} , C–Cl of $\text{Cl}_3\text{C}-$); ^1H NMR, δ 4.0 ppm (s, CH_3-).

The reaction of dichloromethanesulfonyl chloride in the presence of toluenesulfonyl chloride. Toluenesulfonyl chloride (5.2 g, 0.02 mol) in ethyl ether (25 ml) was mixed with triethylamine (2.75 g, 0.02 mol), and dichloromethanesulfonyl chloride (5 g, 0.02 mol) was slowly added. After 1 h at room temperature the ether phase was separated from the oily residue and evaporated *in vacuo* to yield 5.2 g unreacted toluenesulfonyl chloride. The recovered toluenesulfonyl chloride was identified with an authentic sample.

The reaction of dichloromethanesulfonyl chloride with half an equivalent triethylamine. Triethylamine (5.0 g, 0.05 mol) was slowly added to a solution of dichloromethanesulfonyl chloride (18.3 g, 0.1 mol) in ethyl ether (100 ml). The mixture was stirred at room temperature for 1 h. The heavy oil was allowed to separate from the ether solution. Evaporation of the ether solution *in vacuo* yielded half an equivalent unreacted dichloromethanesulfonyl chloride (9 g) which was identified with an authentic sample.

The reaction of dichloromethanesulfonyl chloride in the presence of triethylammonium bromide. Triethylamine (5 g, 0.05 mol) was added for 3 min to a solution of dichloromethanesulfonyl chloride (9.1 g, 0.05 mol) and triethylammonium bromide (0.1 g, 0.05 mol) in chloroform (100 ml). The mixture was stirred for 1 h at 25 °C. A solution of bromine (8.8 g, 0.055 mol) in chloroform (25 ml) and water (75 ml) was then added in one portion with vigorous stirring. The organic layer was allowed to separate after 10 min, and washed with aqueous sodium bisulfite (10 %) to remove excess bromine and then with water. The organic layer was dried and evaporated *in vacuo* to give a semicrystalline residue. Mass spectrum (20 eV, direct inlet) of the crude residue shows the presence of different halomethyl fragments at *m/e* (rel. intensity): CCl_2^+ 117 (100), 119 (96.4), 121 (30.7); BrCl_2C^+ 161 (48.9), 163 (78.1), 165 (35.0), 167 (5.1); Br_2ClC^+ 205 (5.8), 207 (11.7), 209 (9.5), 301 (2.9).

Treatment of trichloromethanesulfinate with triethylammonium bromide. Triethylamine (5.0 g, 0.05 mol) was added to a solution of dichloromethanesulfonyl chloride (9.1 g, 0.05 mol) in chloroform (100 ml). The solution was stirred for 15 min at 25 °C. Triethylammonium bromide (9.1 g, 0.05 mol) was added and the mixture was stirred for an additional hour. A solution of bromine (8.8 g, 0.055 mol) in chloroform (25 ml) and water (75 ml) was then added in one portion with vigorous stirring. The organic layer was allowed to separate after 10 min, and washed with aqueous sodium bisulfite (10 %) to remove excess bromine and then with water. The organic layer was dried and evaporated *in vacuo* to give a semicrystalline residue. Mass spectrum (20 eV, direct inlet) of the crude residue shows the presence of halomethyl fragments at *m/e* (rel. intensity): CCl_2^+ 117 (100), 119 (95.2), 121 (30.6); BrCl_2C^+ 161 (4.5), 163 (6.9), 165 (3.2), 167 (0.5).

Reaction of chloromethanesulfonyl chloride and triethylamine. Triethylamine (3.3 g, 0.033 mol) was slowly added to a cooled solution of chloromethanesulfonyl chloride (5 g, 0.033 mol) in ethyl ether (50 ml). The reaction mixture was stirred for 30 min at room temperature and then extracted with water (100 ml). The aqueous solution was saturated with chlorine and extracted with carbon tetrachloride. Dichloromethanesulfonyl chloride is not obtained in this experiment as shown by NMR analysis. A yield of less than 1 % is detectable which was determined by a reference solution of dichloromethanesulfonyl chloride in CCl_4 .

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