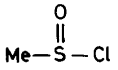
Evidence for Methanethial *S*-Oxide during the Reaction of Methanesulphinyl Chloride and *N*,*N*-Dimethylmethanamide (DMF)

Fillmore Freeman* and Monica C. Keindl

Department of Chemistry, University of California, Irvine, California 92717, U.S.A.

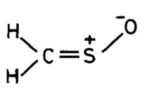
Methanethial *S*-oxide was intercepted as an intermediate during the reaction of methanesulphinyl chloride and *N*,*N*-dimethylmethanamide (DMF), which afforded *S*-methyl methanesulphonothioate and *S*-(chloromethyl) methanesulphonothioate.

Although sulphines may be prepared by the dehydrochlorination of sulphinyl chlorides, oxidation of thiones and thiocarbonyl derivatives, and a variety of other methods,[1,2] none of these procedures has been successful for the synthesis of the parent sulphine, methanethial *S*-oxide (thioformaldehyde *S*-oxide) (**2**). Attempts to prepare (**2**) by the action of triethylamine on methanesulphinyl chloride (**1**) or to intercept it by cycloaddition to enamines[2] or ketene acetals[3] have been unsuccessful.[1,2,4,5]†

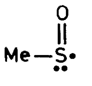


$\mathrm{Me{-}\overset{O}{\overset{\|}{S}}{-}Cl}$

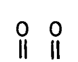
(**1**)



(**2**)



(**3**)



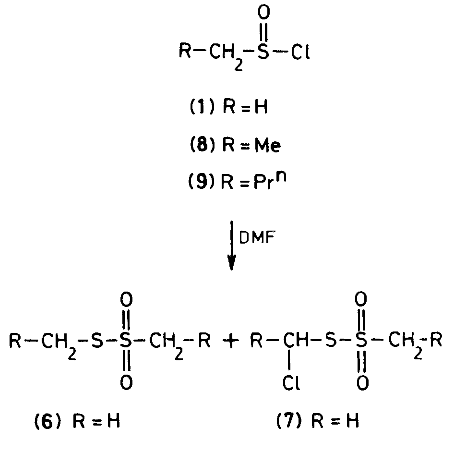
$\mathrm{Me{-}\overset{O}{\overset{\|}{S}}{-}\overset{O}{\overset{\|}{S}}{-}Me}$

(**4**)

$\mathrm{Me{-}\overset{O}{\overset{\|}{S}}{-}O{-}S{-}Me}$

(**5**)

During the course of our studies concerning the detection of sulphinyl radical, *e.g.* (**3**); the elusive transient *vicinal*-disulphoxide, *e.g.* (**4**); and *O*-sulphenyl sulphinate (sulphenic sulphinic anhydride), *e.g.* (**5**), intermediates,[6–9] it was observed that methanesulphinyl chloride (**1**) reacted with anhydrous *N*,*N*-dimethylmethanamide (DMF) under nitrogen to give *S*-methyl methanesulphonothioate (**6**) (11%)[9] and



(**1**) R = H
(**8**) R = Me
(**9**) R = Pr^n

DMF

$$\mathrm{R{-}CH_2{-}\overset{O}{\overset{\|}{S}}{-}Cl} \xrightarrow{\text{DMF}} \mathrm{R{-}CH_2{-}S{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}R} + \mathrm{R{-}\underset{\underset{Cl}{|}}{C}H{-}S{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}R} \quad (1)$$

(**6**) R = H
(**10**) R = Me
(**12**) R = Pr^n

(**7**) R = H
(**11**) R = Me
(**13**) R = Pr^n

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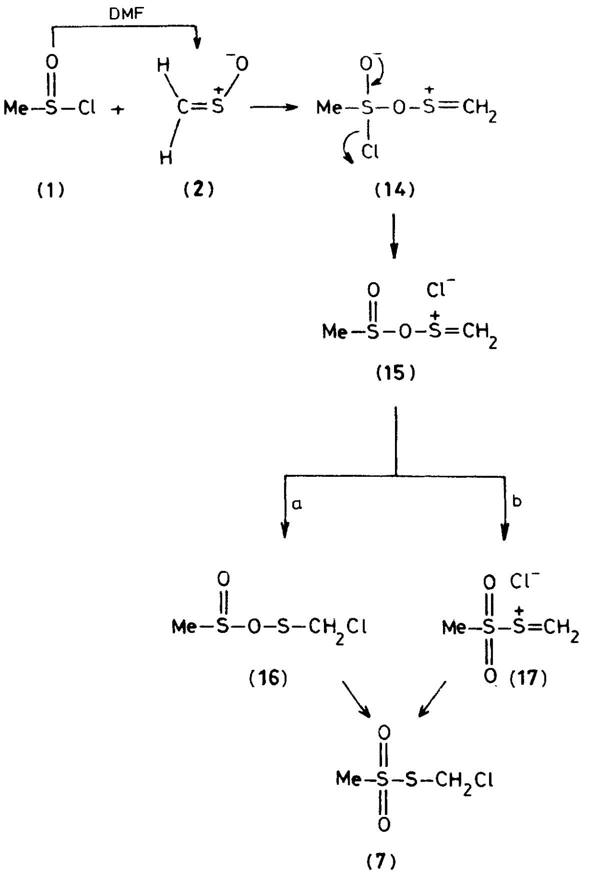
† Elimination of hydrogen chloride from methanesulphinyl chloride (**1**) to give methanethial *S*-oxide (**2**) can be accomplished thermally *via* the flash vacuum pyrolysis technique.[4] Interestingly, (*E*,*Z*)-trimethylsilylmethanethial *S*-oxide is obtained from trimethylsilylmethanesulphinyl chloride and triethylamine.[5]

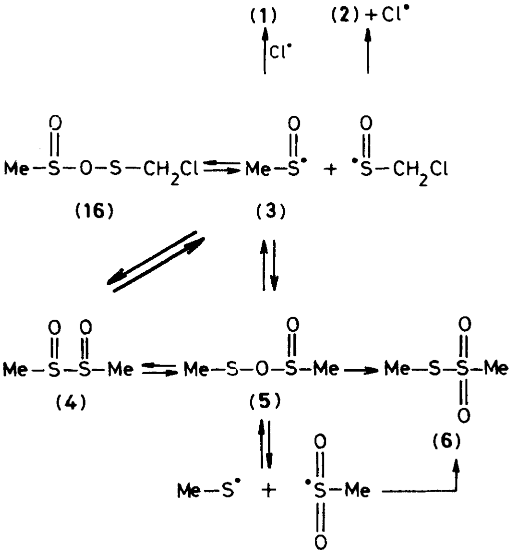


Scheme 1

S-(chloromethyl) methanesulphonothioate (**7**) (63%). Similar results were obtained with ethanesulphinyl chloride (**8**) and n-butanesulphinyl chloride (**9**) which gave *S*-ethyl ethanesulphonothioate (**10**) (18%) together with *S*-(1-chloroethyl) ethanesulphonothioate (**11**) (82%), and *S*-butyl butanesulphonothioate (**12**) (15%) together with *S*-(1-chlorobutyl) butanesulphonothioate (**13**) (85%), respectively, equation (1). The lack of reactivity of benzenesulphinyl chloride and DMF suggests that an α-hydrogen in the sulphinyl chloride is required for the reaction. The thiosulphonate products, which were separated and purified *via* flash chromatography,[9] were characterized by their physical properties, elemental analyses, i.r., ^{1}H and ^{13}C n.m.r. spectroscopy, and chemical ionization and electron impact mass spectrometry.

A reasonable pathway to the thiosulphonate (**7**) involves (**2**) and the intermediate (**14**) (Scheme 1). Nucleophilic attack by (**2**) on (**1**) leads, *via* (**14**), to the intermediate (**15**), which may rearrange to (**16**) or to (**17**). Intramolecular rearrangement of (**16**) or addition of chloride ion to (**17**) affords (**7**). This provides the first direct evidence for the intermediacy of methanethial *S*-oxide (**2**) in solution. Alkanethial *S*-oxides are also involved in the reaction of alkanesulphinyl chlorides (**8**) and (**9**) with DMF. Support for the proposed mechanism in Scheme 1 has been obtained by Block and Bazzi.[5]

The path to *S*-alkyl alkanesulphonothioates (**6**), (**10**), and (**12**) probably involves the respective intermediates (**3**), (**4**), and/or (**5**) (Scheme 2).[7,10]‡ Additional support for the free radical pathway to *S*-methyl methanesulphonothioate (**6**) comes from the reaction of methanesulphinyl chloride (**1**) and DMF which in the presence of the radical inhibitor 1,4-dihydroxybenzene gave only *S*-(chloromethyl) methanesulphonothioate (**7**) (97%).



Scheme 2

This facile reaction of linear alkanesulphinyl chlorides and DMF gives mixtures of *S*-alkyl alkanesulphonothioates (minor products) and *S*-(1-chloroalkyl) alkanesulphonothioates in excellent to quantitative yields. The former are excellent thioalkyl transfer agents[11] and the latter have bactericidal and fungicidal properties.[5,12]

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‡ Diastereoisomeric *vicinal*-disulphoxides (**3**) and *O*-sulphenyl sulphinates (**4**) are possible.