Oxidation of Sulfallate and Related Alkyl Dialkyldithiocarbamates to Dialkylformamides via Sulfine and Iminium Ion Intermediates

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2-Chloroallyl diethyldithiocarbamate (sulfallate herbicide) and related alkyl dialkyldithiocarbamates are converted to the corresponding sulfines (thion S-oxides) on treatment with equimolar m-chloroperoxybenzoic acid (MCPBA) in methanol at -50 °C. These sulfines are moderately stable in methanol but quickly deoxygenate to the parent dithiocarbamates in chloroform or acetone. TLC isolation of products from reaction of sulfallate with excess MCPBA yields 2-chloroallyl disulfide and diethylformamide as major compounds plus small amounts of the thiolcarbamate from desulfuration and m-chlorobenzoic anhydride. Methyl dimethyldithiocarbamate yields dimethylformamide under similar conditions. ^1H and ^{13}C NMR spectroscopy indicates that the principal product in solution from oxidation of alkyl dialkyldithiocarbamates with excess peracid may be the corresponding trialkyl iminium salt, which is suggested to be an appropriate intermediate leading to the compounds ultimately isolated. This peracid system is not a suitable biomimetic model for dithiocarbamates because MCPBA serves not only as an oxidant but probably also as a derivatizing agent for an intermediate(s) in the oxidation sequence.

Biological oxidation reactions are essential activation steps for herbicidal thiolcarbamates on conversion to their sulfoxides (Casida et al., 1974; Schuphan et al., 1981) and for mutagenic 2-chloroallyl thiol- and dithiocarbamates on liberating chloroacroleins following sulfoxidation or S-methylene hydroxylation (Schuphan et al., 1979, 1981). Peracid oxidation of S-(2,3-dichloroallyl) diisopropylthiolcarbamate (diallate) served as a useful biomimetic model for its major initial metabolic reactions (Schuphan et al., 1979, 1981). Preliminary studies (Schuphan et al., 1981) on 2-chloroallyl diethyldithiocarbamate (sulfallate) (1) and related thiocarbamates revealed large differences between mono- and dithiocarbamates in the ability to relate this peracid chemical model to biological conditions. Unusual products from dithiocarbamates are due in large part to formation and further reactions of the corresponding sulfines as detailed in this report.

MATERIALS AND METHODS

Spectroscopy. ^1H nuclear magnetic resonance (NMR) spectra were recorded with a 90-MHz Perkin-Elmer R32B spectrometer for samples in $CDCl_3$ solution with chemical shifts related to internal tetramethylsilane. All coupling constants are reported other than adjacent H–H coupling. ^{13}C NMR spectra were obtained with the UCB-250 (University of California, Berkeley, Chemistry Department) instrument (63 MHz for ^{13}C) for samples in $CDCl_3$ (or CD_3OD or CD_3COCD_3 if specifically indicated) relating the chemical shifts to internal tetramethylsilane and reporting the multiplicity in the proton off-resonance mode. (Abbreviations used are as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = double doublet.) Chemical ionization mass spectrometry (CI-MS) utilized the Finnigan Model 3300 spectrometer with methane as the reagent gas. High-resolution electron impact mass spectrometry (EI-MS) for exact mass measurements was performed in the Mass Spectrometer Laboratory of the Department of Chemistry (University of California, Berkeley).

Chromatography. Thin-layer chromatography (TLC) utilized silica gel F_{254} chromatoplates with 0.25-mm gel thickness for analysis and 1.0 mm-gel thickness for preparative isolations and product visualization with UV light or I_2 vapor.

Chemicals. m-Chloroperoxybenzoic acid (MCPBA) (commercial, 85% assay) was upgraded (99+%) by removing m-chlorobenzoic acid on extracting a dichloromethane solution with a pH 7.5 buffer (Fieser and Fieser, 1967). 2-Chloroallyl diethylthiolcarbamate (**1D**) (Schuphan et al., 1981) was provided by I. Schuphan. Dithiocarbamates 1–7 (Table I) were prepared according to Harman and D'Amico (1959). Several compounds were synthesized to compare with peracid oxidation products of sulfallate as indicated below or in the supplementary material (see paragraph at end of paper regarding supplementary material).

Diethylthioformamide and Its Sulfine and Related Compounds. A benzene solution (30 mL) of diethylformamide (1 g) and P_2S_5 (2.2 g) was refluxed for 10 min. Distillation at 118 °C/12 mmHg gave 1 g (85%) of pure diethylthioformamide: NMR ^1H δ 9.22 (s, 1 H), 3.84 (q, 2 H), 3.54 (q, 2 H), 1.29 (t, 3 H), 1.23 (t, 3 H); NMR ^{13}C δ 186.72 (s), 50.70 (t), 42.30 (t), 14.43 (q), 11.21 (q); NMR ^{13}C (CD_3OD) δ 187.75, 51.59, 42.67, 14.73, 11.32; $(M + 1)^+$, 118. Diethylthioformamide S-oxide was obtained on reacting diethylthioformamide with equimolar MCPBA in $CDCl_3$ or other solvents at -40 °C as indicated: NMR ^1H δ 10.16 (s), 4.11 (q), 3.36 (q), 1.38 (t, 3 H), 1.31 (t, 3 H); NMR ^{13}C δ 165.04 (s), 52.27 (t), 43.89 (t), 14.20 (q), 14.13 (q); NMR δ ^{13}C (CD_3OD) 168.03, 53.57, 44.75, 14.46; NMR ^{13}C (CD_3COCD_3) δ 166.56, 52.78, 44.22, 14.50, 14.45. For comparison the NMR spectral features of diethylformamide are as follows: ^{13}C δ 162.21 (s), 41.92 (t), 36.58 (t), 14.92 (q), 12.83 (q); ^{13}C (CD_3OD) δ 164.21, 43.10, 37.69, 15.03, 12.99. Analogous procedures were used to synthesize and identify dimethylthioformamide, dimethylthioacetamide, and their sulfine derivatives.

Oxidation Reactions. Dithiocarbamates 1–7 react quickly with MCPBA in various solvents (e.g., $CDCl_3$, CD_3OD, and CD_3COCD_3) at temperatures as low as -50 °C. Care should be exercised in carrying out these oxidations, even on a millimole scale, because they are very exothermic. Reactions in $CDCl_3$ were normally made in NMR tubes starting at -50 °C (dry ice–acetone) by taking a spectrum (spectrometer at 40 °C) immediately after adding 1–4 equiv of MCPBA and further spectra on warming up to ambient temperature. In some cases the reaction mixtures were also examined directly by CI-MS and TLC.

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0021-8561/83/1431-0242$01.50/0

Table I. ^{1}H Chemical Shifts ($CDCl_3$) of *S* α Protons of Dithiocarbamates and Their MCPBA Oxidation Products[a]

no.	compound	equiv of MCPBA 0	1[b]	4[c]
1	$(CH_3CH_2)_2NC(S)SCH_2CCl{=}CH_2$[d]	4.31	3.43	4.60
2	(*E*)-$(CH_3CH_2)_2NC(S)SCH_2CCl{=}CHCl$	4.52	3.70	4.67
3	$(CH_3)_2NC(S)SCH_3$	2.64	2.27	2.97
4	$(CH_3CH_2)_2NC(S)SCH_3$	2.64	2.30	3.02
5	$(CH_3CH_2)_2NC(S)SCH_2CH_3$	3.34	2.69	3.61
6	$(CH_3)_2NC(S)SCH(CH_3)C_2H_5$	4.05	2.92	4.09
7	$(CH_3CH_2)_2NC(S)SC(CH_3)_3$	1.65[e]	1.36[e]	1.68[e]

[a] Assignments for other protons are given in the supplementary material. [b] Sulfine derivatives (1A–7A) at −20 °C. [c] Intermediates 1B–7B at 25 °C. [d] Analogous data for $(CH_3CH_2)_2NC(O)SCH_2CCl{=}CH_2$ (1D) are 3.84, 3.90, and 4.39 ppm for 0, 1, and 4 equiv of MCPBA, respectively. [e] Corresponds to the *tert*-butyl methyls.

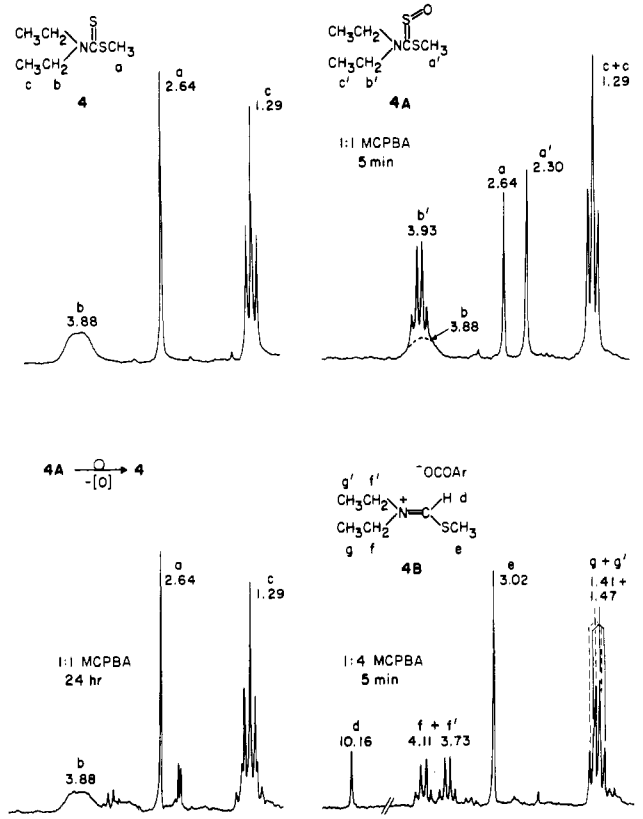


Figure 1. ^{1}H NMR spectra ($CDCl_3$, 25 °C) for methyl diethyldithiocarbamate, 4, for sulfine derivative **4A** from oxidation of 4 with 1 equiv of MCPBA, for **4A** after reversion to 4 on deoxygenation, and for intermediate **4B** from oxidation of 4 with 4 equiv of MCPBA.

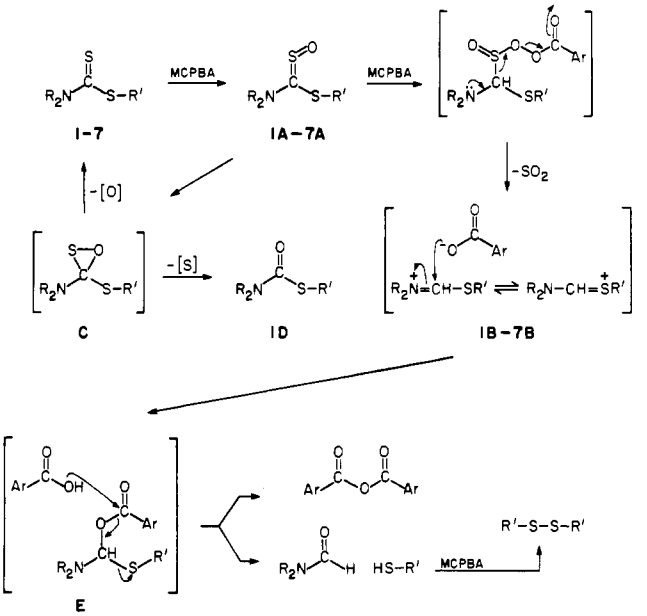


Figure 2. Possible mechanisms for oxidative conversion of sulfallate and alkyl dialkyldithiocarbamates to sulfine derivatives and alkyl dialkylthiocarbamates and of the sulfine derivatives to dialkylformamides and dialkyl disulfides via the trialkyl iminium salt. Ar = 3-chlorophenyl; R = CH_3, C_2H_5; R′ = CH_3, C_2H_5, $CH(CH_3)C_2H_5$, $C(CH_3)_3$, $CH_2CCl{=}CH_2$, and (*E*)-$CH_2CCl{=}CHCl$.

In a typical experiment, 446 mg of 1 (2 mmol) in 2 mL of $CDCl_3$ was added to a stirred and cold (−50 °C) solution of 1.38 g of MCPBA (8 mmol) in 8 mL of $CDCl_3$, maintaining the temperature below −50 °C (dry ice–acetone). The same ^{1}H NMR spectrum was obtained at −50 °C and on warming to 40 °C. After 15 min at room temperature, the contents were cooled again to −30 °C for removing *m*-chlorobenzoic acid on filtration, and the soluble products were separated by preparative TLC (silica–benzene). UV visualization revealed considerable streaking associated with product decomposition during TLC. Identifiable compounds were obtained after recombination and reseparation (silica–chloroform).

RESULTS AND DISCUSSION

Equivalent MCPBA (Figures 1 and 2; Tables I and II). *Products Isolated from Oxidation of Sulfallate and Other Dithiocarbamates.* NMR monitoring revealed that dithiocarbamates 1–7 including sulfallate react quickly with equimolar MCPBA in methanol, chloroform, or acetone at −50 °C. However, only the unmodified dithiocarbamate is obtained on attempted product isolation involving extraction of chloroform solutions with aqueous $NaHCO_3$ or chromatography on silicic acid. Oxidation of sulfallate in the presence of equimolar *p*-toluenesulfonic acid gave thiolcarbamate **1D** as the major product. It appeared, therefore, that an unstable monooxygenated product was quickly formed and readily deoxygenated to the parent compound or desulfurated to the thiolcarbamate, properties characteristic of sulfine derivatives (**1A–7A**) as discussed below.

NMR Spectral Features of Sulfines. Formation of sulfines **1A–7A** results in an upfield shift of all *S*-alkyl protons, the S α protons being affected to the greatest extent (up to 1.1 ppm). This upfield shift is attributable to a weaker electron-withdrawing effect of the C=S=O than of the C=S moiety, noted previously with methyl dithionaphthoate (Zwanenburg et al., 1967b). The oxygen is not attached to the thiol sulfur, in which case there would be a downfield shift of the S α protons (Schuphan et al., 1981). The *S*-(2,3-dichloroallyl) derivative (2) is of particular interest since oxidation at its thiol sulfur would yield an intermediate undergoing a [2,3] sigmatropic rearrangement followed by a 1,2 elimination leading to 2-chloroacrolein (Schuphan et al., 1979, 1981); however, only thion rather than thiol sulfur oxidation occurs with 2 since

Table II. ^{13}C Chemical Shifts of Thiocarbonyl and Neighboring Carbons of Dithiocarbamates and of the Corresponding Carbons in Their MCPBA Oxidation Products

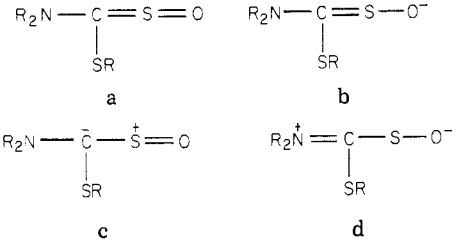
no.	compound and MCPBA equiv[a]	solvent[b]	C=S, C=S=O, or N=CH—S	S C-α	N C-α
1	$(C_2H_5)_2NC(S)SCH_2CCl=CH_2$				
	0	CD_3OD	194.28	45.10	50.75, 47.71
	1:1	CD_3OD	180.75	42.69	45.15
	0	$CDCl_3$	193.63	44.70	49.91, 46.83
	1:1	$CDCl_3$	180.24	42.79	44.68
	1:4	$CDCl_3$	181.21	42.60	55.61, 49.04
	1:4	CD_3COCD_3	181.05	42.20	56.01, 49.89
3	$(CH_3)_2NC(S)SCH_3$				
	0	CD_3OD	199.24	20.54	45.47, 41.51
	1:1	CD_3OD	185.93	19.59	42.24
	1:4	CD_3OD	184.50	17.01	47.73, 42.25
	0	$CDCl_3$	198.26	20.45	45.34, 41.36
	1:1	$CDCl_3$	185.18	17.07	42.29
	1:4	$CDCl_3$	184.60	17.04	49.68, 42.35
5	$(C_2H_5)_2NC(S)SCH_2CH_3$				
	0	CD_3OD	194.88	31.40	49.95, 46.96
	1:1	CD_3OD	180.45	30.79	47.94
	1:4	CD_3COCD_3	182.49	30.40	55.79, 49.31
6	$(CH_3)_2NC(S)SCH(CH_3)C_2H_5$				
	0	CD_3OD	197.00	49.94	45.08, 41.57
	1:1	CD_3OD	183.09	46.07	49.97, 49.18
	1:4	CD_3COCD_3	181.81	49.31	49.71, 42.97
7	$(C_2H_5)_2NC(S)SC(CH_3)_3$				
	0	CD_3OD	194.92	47.48	51.62, 48.04
	1:1	CD_3OD	177.43	44.97	51.61, 51.48
	1:4	CD_3COCD_3	179.95	31.24	56.26, 49.53

[a] Sulfine derivatives (**1A-7A**) at 1:1 MCPBA equiv and intermediates **1B-7B** at 1:4 MCPBA. Other assignments for **1**, **5**, **6**, and **7** and their oxidation products are given in the supplementary material. [b] Reactions were carried out and spectra recorded at −30 °C for CD_3OD and 25 °C for $CDCl_3$ and CD_3COCD_3.

no 2-chloroacrolein is evident by ^1H NMR.

The barrier to free rotation around the C–N bond evident with dithiocarbamates **1–7** at 25 °C is no longer present on introducing the sulfine group. Thus, the two resonance lines for the N α protons of **1–7** collapse to a singlet in **1A–7A**. An *E*/*Z* sulfine isomer mixture is expected to give detectable doubling of the S α protons (Zwanenburg et al., 1967b), but none appears with **1A–7A** down to −30 °C. In spite of the chiral center at the *sec*-butyl group in **6A**, there is still no doubling of the S α proton resonance lines, further indicating the presence of a single sulfine isomer. The (*Z*)-sulfine may be preferred since there is very little change in the chemical shifts of the N α protons in contrast to a significant shift of the S α protons of **1A–7A**.

^{13}C NMR data also support initial C=S rather than thiol sulfur oxidation with equivalent MCPBA. No doubling of any of the ^{13}C lines, as with the ^1H resonances, is observed even down to −90 °C, indicating either a fast interconversion of an *E*/*Z* isomer mixture or more likely that a single isomer is formed. The C=S carbon undergoes a characteristic marked high field shift of 13–17 ppm on conversion to the sulfine (C=S=O); apparently this carbon is affected more than others by the anisotropic effect of the sulfine moiety. This does not appear to be a general phenomenon since either an upfield or downfield shift may occur (Bonini et al., 1973); e.g., we find that thiophosgene (^{13}C δ = 170.28 in $CDCl_3$) resonates at a slightly higher field than its sulfine derivative (172.06 ppm). Sulfine formation with dithiocarbamates leads to an upfield shift of the *S*-alkyl carbons, especially of the S α carbons (1–4 ppm). Sulfoxidation at the thiol sulfur would have led to a downfield shift of the S α carbon (C. Tseng, personal communication). The effect of sulfine formation on the chemical shift of the N α carbons is dependent on the nature of the *S*-alkyl substituent; i.e., a moderate high field shift is found for the nonbranched *S*-alkyls and a small downfield shift when branched alkyls are present. The restricted rotation around the C–N bond that causes the two N α carbons to be fully resolved in dithiocarbamates is almost completely lost on forming the sulfines. The resonance structure most important to the double-bond nature of the C–N bond in dithiocarbamates is presumably much less effective in their sulfines. Hence, in analogy to other sulfines (Zwanenburg et al., 1967a) there may be a strong preference for resonance structure b with an electron deficient sulfinic sulfur atom over d with the double-bond character at C–N.



Synthesis, Stability, and Reactions of Sulfines. Equimolar MCPBA oxidation occurs preferentially or exclusively at the thion sulfur of dithiocarbamates, as is also the case with aryl dithiocarboxylic esters (Zwanenburg and Kiełbasiński, 1979; Zwanenburg et al., 1967b) and thiaxanthion (Strating et al., 1966). This specificity is attributable to the greater polarizability of the C=S function (Zwanenburg et al., 1967a).

Dithiocarbamate sulfines are too unstable to isolate pure by extraction and chromatography on silicic acid at ambient temperatures. Their relative stability and decomposition mechanisms were examined by NMR spectroscopy. Sulfine derivatives of sulfallate (**1A**) and alkyl dialkyldithiocarbamates (**2A–7A**) are stable for a few hours at 25 °C in methanol but undergo rapid spontaneous decomposition in chloroform and acetone. Sulfines **6A** and

7A, with S-alkyl branching, are more stable than 1A–5A and undergo relatively little decomposition in methanol after 3 days at 25 °C. However, they are much less stable than those of aryl dithiocarboxylic esters which are often isolable as E and Z isomers (Zwanenburg et al., 1967b, 1968) and those of S-aryl N-arylthiocarbamates with stabilization from internal hydrogen bonding (Walter and Bode, 1965). Experiments to trap 3A by treatment with CH_3Li (Zwanenburg and Kiełbasiński, 1979) or CH_2N_2 (Zwanenburg and Wegenaar, 1973) were unsuccessful, giving instead facilitated reversion to 3. Sulfines of dialkylthioformamides and dimethylthioacetamide are only detected on oxidations below −30 °C and are therefore even less stable than those of dithiocarbamates.

Dithiocarbamate sulfines (1A–7A) undergo spontaneous decomposition almost exclusively by deoxygenation to the parent compounds. This is contrary to expectations since many other sulfines (including those of dialkylthioformamides and dimethylthioacetamide examined here) decompose only by desulfuration (Hogg, 1977). The rate of deoxygenation of dithiocarbamate sulfines is enhanced with triphenylphosphine, which is converted to triphenylphosphine oxide, as noted also with thioaldehyde S-oxides (Strating et al., 1967). Desulfuration shifts from a very minor to the major pathway for decomposition of sulfines of dithiocarbamates in the presence of p-toluenesulfonic acid; similarly, the formation of H_2S and xanthion from the sulfine of thiaxanthion is enhanced by a trace of H_2SO_4 (Strating et al., 1966). The ability of the sulfine derivatives of dithiocarbamates to extrude either oxygen or sulfur is conveniently rationalized by invoking a cyclic oxathiiran intermediate (C), previously postulated in the photochemical conversion of sulfines to carbonyl compounds (Hogg, 1979).

Excess MCPBA (Figures 1 and 2; Tables I and II). *Products Isolated from Oxidation of Sulfallate and Methyl Dimethyldithiocarbamate.* Reaction of sulfallate with 4 equiv of MCPBA in chloroform and product isolation by TLC (silica/benzene) gave two major compounds [2-chloroallyl disulfide (92%, R_f = 0.84) and diethylformamide (78%, R_f = 0.11)] and two minor products [thiocarbamate 1D (5%, R_f = 0.75) and m-chlorobenzoic anhydride (R_f = 0.37)], each identified by TLC, MS, and ^{13}C and ^1H NMR. Exact mass measurement served to identify the compound present in largest amount (found 213.9443) as the disulfide (calculated 213.9444) rather than another possible product of very similar molecular weight, i.e., bis(2-chloroallyl) sulfone (calculated 213.9622). The other components were evident by CI-MS after isolation or on the reaction mixture itself (M + 1: 102 for diethylformamide; 208 for 1D; 295 for the anhydride). On a similar basis, TLC (silica–benzene) of a reaction mixture of 3 (1 mmol) with excess MCPBA (4 mmol) gave dimethylformamide (M + 1 = 74; R_f = 0.11). NMR spectra of the reaction mixtures were not appropriate for those of the products ultimately isolated. The sulfallate derivative in solution (referred to as "intermediate" 1B) decomposed slowly on washing the chloroform with water or faster on extracting it with aqueous $NaHCO_3$, HCl, $NaHSO_3$, or pyridine. 1B decomposed completely on attempted TLC isolation as noted above.

NMR Spectral Features of Intermediates. The products in solution (1B–7B) from oxidation of 1–7 with excess MCPBA (4 equiv is necessary to drive the reaction to completion) are characterized by the following ^1H NMR spectral changes: a new singlet resonanting at an unusually low field (10.0–10.2 ppm) in addition to the acidic proton of m-chlorobenzoic acid; a downfield shift of the S α protons in contrast to an upfield shift with 1 equiv of MCPBA (Table I); effective restricted rotation around the C–N bond at 25 °C for the N α protons of 1B–7B (e.g., see Figure 1 for 4B in which the 0.38-ppm signal separation for the N α protons indicates their chemical nonequivalence). ^{13}C NMR examination (Table II) reveals a new signal at ~182 ppm which resonates in an upfield shift of 12–15 ppm compared with the C=S carbon in the starting material. This carbon is directly bonded to a proton since the ~182-pm signal is split to two lines in the proton off-resonance mode. The S α carbons in the oxidized materials are shifted upfield by 0.6–16 ppm. The oxidized compounds (B) have a larger separation between the N α carbons (6.5–7.5 ppm) as compared to the analogous carbons in the starting materials (3–4 ppm) at 25 °C.

Possible Nature and Alternative Mechanisms for Formation of Intermediates. 1B–7B are formed on further oxidation of sulfines 1A–7A. Attempted isolation of 1B yields a disulfide, indicating that the S-chloroallyl substitutent is present in 1B as a sulfide or sulfoxide but not a sulfone. The low-field proton of 1B originates from the MCPBA proton since oxidation of 1 with excess MCPBA-d (aryl-CO_3D) results in isolation of diethylformamide-d [$(C_2H_5)_2NC(O)D$].

Figure 2 gives a possible mechanism accommodating the NMR spectral features of the intermediates (i.e., the low-field resonating proton originating from the MCPBA proton, the restricted rotation around the C–N bond, and the upfield shifts of the original C=S and S α-carbons) and the nature of the terminal products. It invokes an iminium ion intermediate with a nonoxidized thiol sulfur. An MCPBA molecule is added across the C=S bond of the intially formed dithiocarbamate S-oxide (A) followed by loss of SO_2 and formation of the iminium ion which might have the appropriate spectral features for intermediate B (Figure 1). The ^1H and ^{13}C NMR parameters reported for N,N,S-trimethyliminium chloride (Rabiller et al., 1977) closely resemble those of the 1:4 oxidation product(s) of 3 (Table II). The iminium salt has the advantage of added stability due to the contribution of the resonance hybrids as illustrated. A dissociation–recombination of the iminium ion pair gives E, which upon reaction with m-chlorobenzoic acid gives the anhydride and dialkylformamide. The alkyl disulfide is formed via oxidation of RSH by excess MCPBA.

An alternative mechanism (Schuphan et al., 1981) is based on an oxidized thiol intermediate, the sulfinyl sulfine [for related compounds, see Zwanenburg et al. (1968)], leading to formation of the dialkylthioformamide sulfine which is stabilized as a complex in solution. This hypothesis was suggested because the low-field proton of 4B (Figure 1) resonates at exactly the same chemical shift (10.16 ppm) as the analogous proton of diethylthioformamide S-oxide and the other relevant ^1H NMR signals are very similar but not identical for these two materials. However, it has several disadvantages. The sulfine of diethylthioformamide per se cannot exist under these conditions; i.e., the pure compound completely decomposes to diethylformamide and elemental sulfur above −30 °C and with excess MCPBA it completely converts to diethylformamide even at −50 °C. In contrast, intermediate 4B is stable in boiling $CDCl_3$ at least for 1 h or at 25 °C for several days. Although an adduct of diethylthioformamide sulfine and a mixed peroxyanhydride may be rationalized as accommodating the spectral data and required stability, the iminium ion hypothesis combines the close agreement of ^1H and ^{13}C spectral data with earlier studies (Rabiller et al., 1977) and a plausible reaction

mechanism for its formation (Figure 2).

Other Oxidants. Sulfallate in $CDCl_3$ at 25 °C did not react with *tert*-butyl benzoylperoxide but did react with several other oxidants. Excess $KMnO_4$ (heterogeneous reactions in $CDCl_3$) was consumed but **1** remained unchanged, perhaps due to slow formation of the sulfine and reversion to starting material. Excess iodosobenzene gave products similar but not identical in ^1H NMR spectral features to those from MCPBA; the differences were in signals associated with the chloroallyl moiety. **1A** was formed with an equivalent amount of the complex of 1,4-diazabicyclo[2.2.2]octane and bromine (Oae et al., 1966) in the presence of equimolar water, probably as a result of bromine addition to the C=S bond followed by oxidative dehalogenation to form the sulfine (Veenstra et al., 1977).

Peracid System as Biomimetic Model. The biological activity of many organosulfur compounds is associated with in vivo oxidation at the sulfur atom to generate a bioactive species, e.g., conversion of phosphorothionates (P=S) to phosphates (P=O). Peracid oxidation mimics this type of biooxidation, since 1 equiv converts the P=S bond to P=O (Eto, 1974). The peracid system is also a suitable model for bioactivation of thiolcarbamates because in this case sulfur oxidation forms carbamoylating agents or initiates a series of reactions leading to 2-chloroacrolein (Casida et al., 1974; Schuphan et al., 1979, 1981). However, it is not appropriate for dithiocarbamates, other than to achieve some degree of desulfuration to thiolcarbamates, because with dithiocarbamates MCPBA serves not only as an oxidant but probably also as a derivatizing agent for an intermediate(s) in the oxidation sequence. Thus, we find that on monoequivalent MCPBA oxidation sulfallate retains its mutagenic activity in the S-9 activated Ames *Salmonella* mutagenicity test as if sulfallate alone was introduced (Rosen et al., 1980), a finding consistent with the chemical results since the sulfine readily deoxygenates to revert to the starting material. However, on oxidation of sulfallate with excess MCPBA there is a complete loss of mutagenic activity, due to extensive breakdown to nonactive fragments.

ACKNOWLEDGMENT

Dr. Chien Tseng (Stauffer Chemical Co., Richmond, California) provided helpful suggestions on possible reaction mechanisms. We thank our laboratory colleagues Dr. Ingolf Schuphan, Dr. Luis Ruzo, and Ellen Kimmel for assistance or comments. Rudy Nunlist and Richard Mazzarisi (NMR Laboratory, Department of Chemistry, University of California, Berkeley) assisted in obtaining NMR spectra.

Registry No. 1, 95-06-7; **1A**, 83966-64-7; **1B**, 83966-66-9; **2**, 83966-61-4; **2A**, 83966-67-0; **2B**, 83966-69-2; **3**, 3735-92-0; **3A**, 83966-70-5; **3B**, 83966-71-6; **4**, 686-07-7; **4A**, 83966-72-7; **4B**, 83966-74-9; **5**, 4740-11-8; **5A**, 83966-75-0; **5B**, 83966-77-2; **6**, 83966-62-5; **6A**, 83966-78-3; **6B**, 83966-80-7; **7**, 83966-63-6; **7A**, 83966-81-8; **7B**, 83966-83-0; MCPBA, 937-14-4; 2-chloroallyl mercaptan, 18616-08-5; 2-chloroallyl disulfide, 83983-95-3; bis(2-chloroallyl) sulfide, 4162-53-2; bis(2-chloroallyl) sulfone, 4162-54-3; diethylthioformamide, 13839-14-0; diethylformamide, 617-84-5; 2-chloroallyl chloride, 78-88-6; diethylthioformamide *S*-oxide, 83966-84-1.

Supplementary Material Available: NMR spectral data supplemental to those in Tables I and II. Syntheses and spectral data for dithiocarbamates, 2-chloroallyl mercaptan and disulfide, and bis(2-chloroallyl) sulfine and sulfone (3 pages). Ordering information is given on any current masthead page.

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Received for review March 1, 1982. Revised manuscript received October 11, 1982. Accepted October 26, 1982. This study was supported in part by the National Institute of Environmental Health Sciences (Grant PO1 ES00049). In memory of Dr. Itshak Granoth, Sept 6, 1941–July 20, 1981.