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[2,3] SIGMATROPIC REARRANGEMENT OF S-(3-CHLOROALLYL) THIOCARBAMATE SULFOXIDES FOLLOWED BY A 1,2-ELIMINATION REACTION YIELDING UNSATURATED ALDEHYDES AND ACID CHLORIDES

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Summary. Peracid oxidation of S-(2,3-dichloroallyl) and S-(2,3,3-trichloroallyl) thiocarbamates yields 2-chloroacrolein and 2-chloroacrylyl chloride, respectively, via intermediate S-allyl thiocarbamate sulfoxides and S-O-allyl thiocarbamate sulfenate esters.

In our continuing studies[1-5] to understand the metabolism and mode of action of herbicidally-active thiocarbamates, we recently synthesized a new class of 2- and 2,3-chlorinated S-allyl thiocarbamate sulfoxides 2. These unsaturated carbamoyl sulfoxides are unstable and within one hr at 25° they undergo a [2,3] sigmatropic rearrangement possibly via 3 followed, in the cases of A-C, by an elimination reaction. The first process involves a wholly concerted thermal rearrangement, analogous to the reversible rearrangement of p-tolyl allyl sulfoxide[6-8], to give the unstable S-O-allyl thiocarbamate sulfenate esters 4A-C. The second reaction involves a 1,2-elimination giving an unsaturated aldehyde 5H or acid chloride 5(Cl) in quantitative yield along with a carbamoylsulfenyl chloride 6.

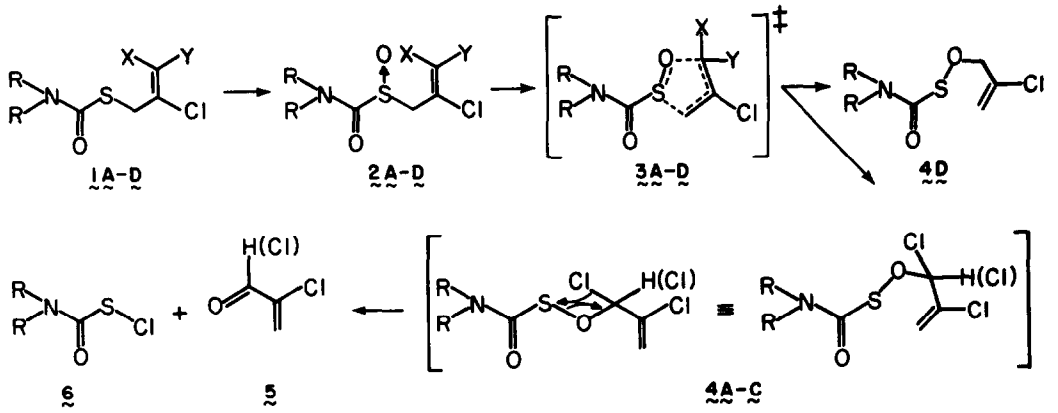

Figure. Sulfoxidation of S-(chloroallyl) N,N-dialkylthiocarbamates (1) followed by a [2,3] sigmatropic rearrangement of the sulfoxides (2) examined with four compounds (A-D).
A: R=$(CH_3)_2CH$-, X=H, Y=Cl (cis-diallate). B: R=$(CH_3)_2CH$-, X=Cl, Y=H (trans-diallate).
C: R=$(CH_3)_2CH$-, X=Cl, Y=Cl (triallate). D: R=CH_3CH_2-, X=H, Y=H.

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The previously-known sulfoxides of S-alkyl and S-benzyl thiocarbamates are adequately stable for preparation and isolation at room temperature[9-11], whereas sulfoxides 2A-C of the isomers of S-(2,3-dichloroallyl) N,N-diisopropylthiocarbamate 1A-B and of S-(2,3,3-trichloroallyl) N,N-diisopropylthiocarbamate 1C are only isolatable by working at low temperature. We synthesized the unsaturated compounds by a previously-described method[11] in which equimolar amounts of the thiocarbamate and m-chloroperoxybenzoic acid (MCPBA) are reacted in CH_2Cl_2 or $CDCl_3$ at -15°; however, the procedure was modified by maintaining the temperature below 0° for workup. Purified cis-diallate[12] 1A was shown in time-dependent NMR studies[13] to be oxidized approximately 10-times faster than the trans-isomer 1B or triallate 1C. The identity of sulfoxides 2A-C is established by NMR spectroscopy (Table) which mainly shows all signals at lower field compared with the parent compounds. The methyl group protons of the two diisopropyl moieties appear as four doublets as a result of both the chiral center at sulfur and restricted rotation around the amide N-CO bond, as noted previously for saturated S-alkyl thiocarbamate sulfoxides[10,14]. With the parent thiocarbamates, however, the methyl group signals appear as one doublet at 40° (Table) but two doublets are evident at 0° due to restricted rotation around the amide bond. The IR spectra also show the characteristic S=O absorption band at 1070 cm^{-1}, which is not present in the spectrum of the parent compound[14,15]. Finally, reaction of thiocarbamates 1A-C or their sulfoxides 2A-C with excess MCPBA converts them to the corresponding sulfones, identified by NMR and MS[16].

Table. NMR Chemical Shifts (ppm) in $CDCl_3$-TMS at 40°. For structures see the figure. Proton-proton coupling in Hz: $(CH_3)_2$-CH, 6.65 in all cases; CH_2-C=CH, < 0.9 for 1A, 1B and 2A; CH_3-CH_2; 7.10 for 1D and 4D; =CH_2, 1.1 for 1D and < 1.0 for 4D. Abbreviations: s = singlet, d = doublet, t = triplet, qa = quartet, qi = quintet, m = multiplet, br = broad.

		R		-CH_2C(Cl)=CXY	
Cmpd		CH_3	-CH_2- or >CH-	-CH_2-	=CH- or =CH_2
1	A	d,1.30	br m,3.82	d,3.86	t,6.52
	B	d,1.31	br m,3.82	d,4.06	t,6.23
	C	d,1.31	br m,3.82	s,4.13	-
	D	t,1.18	qa,3.40	s,3.84	2d,5.26,5.48
2	A	4d,1.27,1.30, 1.42,1.46	2m~qi,3.60, 4.36	d,3.89	t,6.53
	B	4d,1.28,1.30, 1.44,1.47	2m~qi,3.60, 4.35	d,4.10	t,6.54
	C	4d,1.27,1.30, 1.45,1.47	2m~qi,3.61, 4.37	d,4.16	-
	D	m,1.26	m,3.49	s,3.90	s,5.55
4	D	t,1.18	qa,3.18	s,4.48	2d,5.45,5.53

cis-Diallate sulfoxide 2A in $CDCl_3$ degrades completely within 10 min at 40°; the reaction rate of 2A is about 10-times faster than that of trans-diallate sulfoxide 2B or triallate sulfoxide 2C. Both 2A and 2B react quantitatively to give an unsaturated aldehyde readily

evident from the time-dependent buildup of an aldehyde proton signal at δ 9.46 along with formation of a double doublet at δ 6.43 and 6.59. Decomposition of 2C is conveniently monitored by the formation of a double doublet at δ 6.44 and 6.92. IR[15], CI-MS[16] and independent synthesis[17,18] establish the structure of the relevant compounds as 2-chloroacrolein 5H and 2-chloroacrylyl chloride 5(Cl). N,N-Diisopropylcarbamoylsulfenyl chloride 6, evident immediately after spontaneous decomposition of the sulfoxides of both diallate isomers and of triallate, is identified by NMR and its $[M+1]^+$ ions in CI-MS, as well as by its addition product to cyclohexene[19] and independent synthesis[19,20]. Compound 6 is also unstable in $CDCl_3$ and decomposes over several hr at 40° to yield N,N-diisopropylcarbamoyl chloride, sulfur and diisopropylamine hydrochloride; this is reasonable since carbamoylsulfenyl chlorides are known to degrade at room temperature releasing sulfur[19,20] and the carbamoyl chloride which, with traces of water, gives the dialkylamine hydrochloride.

The rearrangement mechanism is established as a two-step process by following the oxidation of a S-(2-chloroallyl) thiocarbamate 1D, with no chlorine atom in the 3 position. Oxidation of 1D with equimolar MCPBA at -15° in $CDCl_3$ yields a moderately stable sulfoxide 2D which, like the sulfoxides of diallate and triallate, is easily purified by aqueous sodium carbonate extraction at 0°. However, within 30 min at 40° 2D undergoes quantitative rearrangement to yield the stable sulfenate ester 4D. No formation of an aldehyde is observed. The CI-MS data for 4D show intense $[M+1]^+$ ions which is not the case for any previously-known thiocarbamate sulfoxide[14]. NMR data at different temperatures show no equilibration between 4D and its sulfoxide. Even without direct spectral evidence for 4A-C, the finding of 4D as a stable compound is considered adequate for proposing the analogous compounds 4A-C as intermediates in decomposition of diallate and triallate sulfoxides.

Certain NMR spectral changes (Table) occurring on sulfoxidation possibly reflect dynamic processes. Thus, on oxidation of 1D to 2D, the two doublets of the terminal methylene group are unexpectedly converted to a singlet. There is an analogous change on oxidation of 1A and 1B; the cis-trans protons (X and Y in Figure) become equalized on forming their respective sulfoxides 2A and 2B.

The newly-observed two-step rearrangement process of S-(3-chloroallyl) or S-(3,3-dichloroallyl) thiocarbamate sulfoxides reveals a new synthetic method for the preparation of substituted acroleins or acrylyl chlorides, respectively, in nearly quantitative yields for the examples given. Reaction of this class of thiocarbamates or their sulfoxides with lithium diisopropylamide followed by an alkylation reaction should lead, on spontaneous rearrangement of the sulfoxide and elimination, to a variety of unsaturated aldehydes or acid chlorides; analogous alkylations followed by rearrangements are known with phenyl allyl sulfoxides[21,22] and dithiocarbamates[23].

Caution: Diallate is metabolized by hepatic liver enzymes, probably oxidases, to unidentified product(s) which are potent mutagens in bacterial assays, particularly with the TA100 strain of Salmonella typhimurium[24,25]. It is of interest, as we will detail elsewhere, that both diallate sulfoxide and 2-chloroacrolein are highly mutagenic in the same assay system, giving 1000-2000 revertants per μg.

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