Sulfur Dichloride Diadducts of Unsaturated Fatty Derivatives. I. Preparation and Oxidation

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Abstract

Sulfur dichloride diadducts of oleate esters, oleylnitrile, elaidate esters and ethyl linoleate were prepared by addition of the theoretical amount of sulfur dichloride to the fatty derivative. Similar diadducts were also prepared from commercial oleate esters including esters of ADM's monoenoic acid. Several of the resulting β,β'-dichlorosulfide diesters were then oxidized with peracetic acid to β,β'-dichlorosulfoxide diesters and to β,β'-dichlorosulfone diesters. The latter materials were converted to the divinyl sulfone diacids.

Cis and *trans*-2-butene were used as model compounds for studying the addition of sulfur dichloride to oleates and elaidates respectively. The results on these systems, which paralleled the results with the fatty materials, indicated that substitution reactions were negligible and that the addition was stereoselective, that is, oleates and elaidates gave stereochemically different products.

Introduction

THE SULFANES ARE A FAMILY of compounds of sulfur and chlorine with the general formula, ClS_nCl (13). The simplest two members of the sulfane family, sulfur dichloride, ClSCl, and sulfur monochloride, ClSSCl, are known to react readily with olefins (7–9,23). Perhaps the most studied example of the sulfane-olefin reaction is the synthesis of mustard gas from sulfur monochloride and ethylene (18). This reaction is an example of a system wherein sulfur monochloride apparently disproportionates (4) to sulfur and sulfur dichloride, the latter material then adding to the olefin to form a β,β'-dichlorosulfide. However sulfur monochloride does not always disproportionate before it adds to olefins and, in fact, it usually reacts to

$$S_2Cl_2 \rightleftharpoons SCl_2 + S$$
$$SCl_2 + 2CH_2 = CH_2 \longrightarrow$$
$$Cl{-}CH_2{-}CH_2{-}S{-}CH_2CH_2Cl$$

form mixtures of sulfide and disulfide products (20).

Various fatty oils have been reacted with sulfur dichloride, sulfur monochloride and pentasulfur dichloride (ClS_5Cl). Polyunsaturated oils, in particular olive oil and peanut oil (19), underwent considerable increases in viscosity upon addition of sulfur monochloride and eventually gelled. When films of various oils were exposed to sulfur chloride vapors (11), irregular increases in film weight indicated that the reaction was not simple. However, this reaction has been used to increase the rate of cure of protective oil coatings (2,14). Addition of sulfur chlorides to oils in bulk gave products useful as lubricating oil additives (3), cutting oils (6) and plasticizers (1,12). Highly unsaturated natural oils, when treated with sulfur monochloride in the presence of sodium bicarbonate (21,24), gave flexible foams.

Our interest in the reaction of sulfur dichloride with fatty derivatives was twofold:

1) Since sulfur dichloride was the simplest of the compounds of sulfur and chlorine, we thought it offered the best chance of forming simple, well-defined products with unsaturated fatty materials. We also wanted to study some of the reaction variables in order to learn if the reaction could be controlled to give well-defined adducts.

2) Simple sulfur dichloride-olefin diadducts, $\beta,'\beta$-dichlorosulfides, undergo reactions with nucleophiles more readily than the corresponding alkyl halides. Since fatty chlorides in which the chloride group is near the center of the chain undergo substitution reactions poorly (22) we thought the sulfur dichloride adduct might provide a fatty material with internal chlorine atoms susceptible to reaction with nucleophiles. Accordingly we decided to study the preparation of the sulfur dichloride adducts of oleate and elaidate esters, oleylnitrile and linoleate esters. We also studied the adducts formed from *cis*-2-butene and *trans*-2-butene as models for oleate and elaidate respectively.

Experimental

The ethyl oleate used in this work (97% C 18:1, 1% *trans*) was prepared from high purity oleic acid supplied by the Arizona Chemical Company. Methyl oleate (95% C 18:1, 6% *trans*) was prepared from commercially available methyl oleate by distillation on a 40-plate spinning band column. Isopropyl elaidate (98% C 18:1) was obtained from elaidic acid prepared according to a known procedure (10). Among other esters used were samples prepared from commercially available octadecenoic acid (ADM, 95% C 18:1, 35% *trans*) in which the double bonds are located mainly in the C-7 to C-13 part of the chain. Oleylnitrile (92% C 18:1, 7% C 18:2) was obtained from a commercial sample by distillation on a spinning band column. Ethyl linoleate (97%) was prepared from a sample of linoleic acid (95+%) supplied by the USDA Northern Regional Laboratory. Other commercial materials were used without further purification.

The sulfur dichloride was mixed with phosphorus trichloride (1% v/v) and distilled into a dry-ice-cooled receiver immediately before use. The fraction boiling at 59C–60C was used. Careful distillation of the sulfur dichloride immediately prior to use is recommended in order to minimize the formation of colored products.

The molecular weights reported below were determined by vapor pressure osmometry. Most preparative procedures were similar so only representative examples are shown below.

Bis-9(10)-[ethyl-10(9)-chlorooctadecanoate]-sulfide

A 3-necked 3-liter flask was covered with aluminum foil to exclude light and was fitted with a stirrer, a dry-ice-jacketed addition funnel and a long stem thermometer. Into the flask was placed ethyl oleate

(661 g, 2.13 moles) and anhydrous ether (500 ml) and the solution was cooled to −5C in an ice-salt bath. Freshly distilled sulfur dichloride (105.6 g, 1.06 moles) was then added from the dry-ice-cooled addition funnel into the vigorously stirred solution in the flask. The rate of addition was controlled so that a temperature of −5C to 0C was maintained.

After addition was complete in 90 min, the solution was stirred at 0C for one hour. The solution was then washed twice with cold water, twice with cold 5% sodium bicarbonate solution and again with water. The solution was then dried over anhydrous sodium sulfate, filtered and concentrated under vacuum to give a yellow oil with a Gardner 2 color. Decolorization with charcoal and other filtration gave a pale yellow oil (708 g, 92% of theoretical) with a Gardner 1-minus color and a slightly acrid odor.

Anal. Calc. for $C_{40}H_{76}Cl_2O_4S$: S, 4.4; Cl, 9.8; MW, 724
Found: S, 4.5; Cl, 9.6; MW, 690

In subsequent experiments the water and bicarbonate washes were omitted. The solution was concentrated under vacuum and kept at 0.05 mm for several hours. Part of a diadduct from methyl oleate was crystallized from hexane to give an odorless white solid, mp 43–45C.

Anal. Calc. for $C_{38}H_{72}Cl_2O_4S$: C, 65.6; H, 10.4; Cl, 10.2; S, 4.6
Found: C, 65.7; H, 10.4; Cl, 10.5; S, 4.6

Using this route, we prepared sulfur dichloride diadducts from propyl and isopropyl esters of ADM monoenoic acids, from Emery 2301 methyl oleate and propyl esters of Emery 233LL and 3528R oleic acids, from isopropyl elaidate and from ethylhexyl oleate. All products were pungent yellow oils at room temperature. Most of the subsequent oxidation or substitution reactions were carried out on one or more of these diadducts.

Bis-2-(3-chlorobutyl)-sulfide

A 500 ml 3-necked flask was fitted with a dry-ice-cooled addition funnel, a dry-ice-cooled condenser and a stirrer. After the flask was placed in a methanol-ice bath (−30C), anhydrous ether (200 ml) and *cis*-2-butene (99+%, 27.9 g, 0.5 moles) were added. Freshly distilled sulfur dichloride (26.6 g, 0.26 moles) was then added dropwise while the temperature was maintained below 0C.

After the sulfur dichloride was added, the solution was allowed to stand for 30 min. It was concentrated to a pale yellow liquid that was distilled under vacuum, bp 65–75C (most 72–75C) at 1.25 mm. The resulting product was a pale yellow liquid (46 g, 85% of theoretical). The mobile pot residue also appeared to be product but was not collected. The NMR spectrum of the product had multiplets at δ 4.15 ppm (9 peaks, rel int 1.0) and at 3 ppm (8 peaks, rel int 1.0) and three doublets from 1.2–1.6 ppm (rel int 5.96).

Anal. Calc. for $C_8H_{16}Cl_2S$: S, 14.9; Cl, 33.0; MW, 215
Found: S, 14.4; Cl, 31.7; MW, 223.

The corresponding compound was prepared from *trans-2* butene. The NMR spectrum of this compound had apparent quintets at δ 4.05 ppm (rel int 1.0) and 3 ppm (rel int 1.0) and three doublets from 1.2–1.6 ppm (rel int 6.0).

Anal. Found: S, 14.3; Cl, 32.7; MW, 229.

Bis-9(10)-[methyl-10(9)-chlorooctadecanoate]-sulfoxide

A sample of the corresponding sulfide (25 g, 0.036 moles) was mixed with glacial acetic acid (100 ml) and 35% hydrogen peroxide (3.6 g, 0.036 moles). The resulting solution was heated to 50–60C for 2 hours and allowed to stand at room temperature overnight.

After the solution was tested with starch-iodide paper and was found to be free of active oxygen it was mixed with salt water. The resulting oil was extracted into ether. The ether solution was washed with water until neutral, dried over magnesium sulfate and concentrated to an oil (24.5 g, 96%) that partially crystallized. Recrystallization at −25C from hexane (6 ml of hexane per gram of solid) gave off-white needles, (9 g) mp 76.6–78.5C.

Anal. Calc. for $C_{38}H_{72}Cl_2O_5S$: C, 64.1; H, 10.1; Cl, 10.0; S, 4.5; MW, 712
Found: C, 64.1; H, 10.1; Cl, 9.8; S, 5.0; MW, 685.

The infrared spectrum shows a strong new band at 1040 cm^{-1} that is typical of sulfoxides. The rest of the sample remains an oil that has the band at 1040 cm^{-1}. It appears to be mainly the sulfoxide as shown by TLC (benzene-ether; 1:1 v/v) and (ethanol-ammonium hydroxide; 27:1 v/v).

Bis-9(10)-[ethyl-10(9)-chlorooctadecanoate]-sulfone

The corresponding sulfide (100 g, 0.138 moles) was dissolved in glacial acetic acid (500 ml) and stirred. To this solution was added a mixture of 35% hydrogen peroxide (30 g, 0.31 moles) in glacial acetic acid (50 ml) and the resulting milky solution was heated to 65C. Eventually the solution became clear and nearly colorless. The solution was heated for a half hour after clearing and allowed to cool.

The product was isolated by diluting the reaction mixture with water and extracting the resulting oil with hexane. The hexane extract was washed until no more active oxygen remained, dried over anhydrous sodium sulfate and concentrated to an off-white oil.

Anal. Calc. for $C_{40}H_{76}Cl_2O_6S$: S, 4.2; Cl, 9.3; MW, 755
Found: S, 4.1; Cl, 9.2; MW, 691.

The infrared spectrum of this material had new adsorptions at 1135 cm^{-1} and 1305 cm^{-1} that are typical of sulfones.

Bis-9(10)-[9-octadecenoic acid]-sulfone

A sample of the above sulfone (20 g, 0.027 moles) was dissolved in ethanol (50 ml), mixed with 10% sodium hydroxide solution (200 ml) and the resulting deep burgundy solution heated at 50C for 4 hr. The burgundy color faded to orange. The reaction mixture was allowed to cool and it was acidified with hydrochloric acid. The solution became pale yellow and an oil began to separate. The solution was extracted with ether and the extracts were washed with water, dried over sodium sulfate, decolorized with charcoal, filtered and concentrated under vacuum. Routine filtration of the resulting oil (14 g) through a fritted funnel induced crystallization. Recrystallization of this material from hexane gave a white powder, mp 63C–66C.

Anal. Calc. for $C_{36}H_{66}O_6S$: C, 68.7; H, 10.5; S, 5.1
Found: C, 68.6; H, 10.3; S, 5.3

The NMR spectrum of this material exhibits a triplet at δ 5.95 ppm as would be expected for the methylene-flanked vinyl protons. A small peak at 1627 cm^{-1} in the infrared spectrum is also typical of an olefinic bond. The iodine value of this compound was found to be 0.79 as compared to a sample of divinyl sulfone, 1.98.

The mother liquor from the above crystallization was concentrated to a yellow oil. Its NMR spectrum indicated the presence of ether and ester linkages.

Oleylnitrile-Sulfur Dichloride Adduct

A solution of oleylnitrile (16.9 g, 0.064 moles) and ether (20 ml) was stirred magnetically and was cooled to −10C in an ice-salt bath. Freshly distilled sulfur dichloride (3.3 g, 0.032 moles, 1.98 ml) was then added over a period of 15 min. The reaction mixture was allowed to warm slowly and was concentrated under vacuum to a yellow oil (19.8 g, theory 20.2 g).

Anal. Calc. for $C_{36}H_{66}Cl_2N_2S$: S, 5.09; Cl, 11.3
Found: S, 4.5; Cl, 10.2

The low analytical values in this experiment probably resulted from difficulty in handling small amounts of sulfur dichloride. Sulfur dichloride has a high vapor pressure and undoubtedly some was lost in transferring the small amount. The infrared absorption of this sample at 2250 cm^{-1} indicates the cyano group is still intact.

Ethyl Linoleate-Sulfur Dichloride Adducts

Into a 3-liter 3-necked flask was added anhydrous ether (1200 ml) and the air space remaining was filled with dry nitrogen. A stirrer was fitted in the center neck and a dropping funnel was placed in each side neck.

Ethyl linoleate 97% pure by VPC (19.4 g, 0.0630 moles) was dissolved in ether (10 ml) and placed in one addition funnel. Sulfur dichloride (freshly distilled 6.5 g, 4.01 ml, 0.0631 moles) was placed in the other addition funnel.

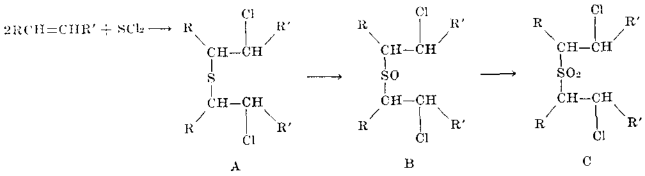
The ether was cooled in an ice bath. One third of the linoleate solution was added. Then, dropwise, 1 ml of sulfur dichloride was added. Another third of the linoleate solution, etc., until addition was complete. Addition took about 20 min. The flask was removed from the ice bath and allowed to warm to room temperature for an hour when the reaction mixture was concentrated under vacuum to a yellow oil. This was filtered through a fritted glass funnel and stored at 0.05 mm for several hours. A viscous dark yellow oil formed. After several days at room temperature this sample was very dark in color. It was decolorized with charcoal to give a stable orange oil.

Anal. Calc. for $C_{20}H_{36}O_2Cl_2S$: Cl, 17.2; S, 7.8; MW, 411 (cyclic product), infinite (polymeric product).
Found: Cl, 15.0; S, 6.9; MW, 668.

Thin-layer chromatography of the reaction mixture in benzene-pyridine (100:5, v/v) showed that the product contained two major components.

Discussion

Sulfur dichloride has been found to add to the double bonds of the oleate derivatives and of the 2-butenes to give the β,β′-dichlorosulfide derivatives, A. These derivatives in turn can be oxidized to the corresponding β,β′-dichlorosulfoxides, B, and the β,β′-dichlorosulfones, C.



$R{=}R' = CH_3$
$R{=}CH_3(CH_2)_7{-}$ or $-(CH_2)_7COOR$, $-(CH_2)_7CN$ when
$R' = -(CH_2)_7COOR$, $-(CH_2)_7CN$ or $CH_3(CH_2)_7{-}$ respectively.

Best results are obtained with the pure monounsaturated fatty derivatives and with the 2-butenes. Fatty materials containing from 80%–85% monounsaturated and from 5%–10% diunsaturated chains form diadducts with a definite yellow color and fair storage stability in a closed bottle at room temperature. Linoleate esters also undergo reaction, but even when the reaction is run under dilute conditions, dark yellow oils result that undergo rapid initial discoloration. Thus the color of the final product apparently depends upon the linoleate content of the starting material as well as on other variables such as the temperature of addition and the purity and amount of sulfur dichloride added.

The formation of strongly colored products from the linoleates is not clearly understood. Possibly the high susceptibility of linoleates to radical reactions results in the formation of hydrogen chloride which, in turn, causes degradation of the product. The reaction of sulfur dichloride with linoleates can give either cyclic products by intramolecular condensation, as recent results on 1,4-diolefins indicate (5), or polymers by intermolecular condensation. The TLC behavior and molecular weight measurements of the sulfur dichloride-linoleate adduct suggest that the intramolecular condensation products are the main products but the reaction needs further study.

The color of the reaction products also depends on the temperature maintained during the addition. Addition of sulfur dichloride to 98% C 18:1 esters at 25C results in an orange adduct that becomes nearly black within a few days. A similar reaction run at −5C to 0C gives a light yellow, fairly stable oil. This result parallels that observed in the addition of chlorine to fatty materials. In systems where addition and substitution reactions are competing, such as in chlorination (16), the substitution reaction and the accompanying hydrogen chloride production can be nearly eliminated if the reaction is run at below zero temperatures. Accurate control of the amount of sulfur dichloride added is also important. Samples prepared with a slight excess of sulfur dichloride underwent rapid and extensive discoloration with the evolution of foul-smelling, fuming gases.

Once formed, the β,β′-dichlorosulfides show reasonable thermal stability. The sulfur dichloride-butene diadducts are distillable under vacuum without decomposition. The oleate diadducts have too high a molecular weight to distill without decomposition, but differential thermal analyses show little heat loss or gain until 200C where a strongly endothermic reaction occurs. This result correlates with observations on a bulk sample in a capillary. The sample yellows but does not undergo rapid decomposition until 200C when an acidic gas, probably hydrogen chloride, is evolved. Upon standing at room temperature in a closed bottle for 1–2 months, representative samples of β,β'-dichlorosulfide diesters did become darker in color. The corresponding sulfones do not undergo rapid decomposition until heated to 250–300C and they appear to be stable indefinitely at room temperature. In general, conversion of an oleate-sulfur dichloride diadduct to either a sulfoxide, sulfone or to a derivative wherein the chlorine atoms are removed results in a markedly more stable compound.

Oxidation of the β,β'-dichlorosulfide diester with one equivalent of peracetic acid yields the sulfoxide and with two or more equivalents, the sulfone. The elemental analyses of these oxidized materials indicate that the oxidation proceeds without loss of the chlorine atoms (8). Temperatures from 50C–70C appear to be the most convenient temperatures to use in these oxidations, but temperatures as high as 100C are satisfactory if care is taken to remove the products as soon as oxidation is complete to prevent yellowing. Oxidation of the sulfide to the sulfone usually results in a bleaching of from 1–2 Gardner units and the β,β'-dichlorosulfone diester is usually an off-white oil.

Substitution reactions did not seem to be occurring in the addition of sulfur dichloride to oleates at −5C to 0C. Evidence in support of this statement is the failure to observe the evolution of significant amounts of hydrogen chloride from the reaction mixtures and the elemental analyses of the products. If substitutions do occur during the reaction of an olefin with sulfur dichloride, other products, in particular, allylic halides and other unsaturated materials are expected. In principle, NMR should be able to detect these added structural features. In practice, unless substitution is an important reaction, the relative concentration of these groups is so low as to make them undetectable in a fatty molecule. Accordingly we decided to study simple models for oleates and elaidates, i.e. *cis* and *trans*-2-butene. The sulfur dichloride-2-butene diadducts are formed in good yield and are easily purified by vacuum distillation. The NMR spectra of these diadducts indicate no olefinic absorptions, no methylene absorptions (allylic) and only what appear to be the nearly expected ratios of methyl group and tertiary hydrogen atom absorptions. Therefore, substitution reactions are negligible in the butene systems, and should also be negligible in the fatty systems.

Cis and *trans*-2-butene do not give identical adducts with sulfur dichloride as shown by the NMR spectra. Recent work indicates that sulfur dichloride adds *trans* to a double bond (15). Our results agree that the reactions is stereoselective but we are unable to say what kind of addition is observed. By *trans* addition, each 2-butene can add to sulfur dichloride to give 3 nonsuperimposable products. As can be seen if the structures are drawn out, the adducts of *cis*-2-butene are configurationally different from the adducts of *trans*-2-butene. The hydrolysis products of these diadducts also suggest a configurational difference and indicate that it is also present between the oleate and elaidate diadducts. The reactions of the sulfur dichloride adducts with various nucleophiles will be reported in a later paper.

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