Hydrogen Sulfide Adducts of Methyl *trans,trans*-9,11-Octadecadienoate

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ABSTRACT

Hydrogen sulfide was added to methyl *trans,trans*-9,11-octadecadienoate in benzene solution at 25 C with ultraviolet radiation. GC-MS and GLC analysis of the reaction product showed the presence of methyl oleate, methyl stearate, geometric isomers of methyl 9,11-octadecadienoate, methyl 9,12-epoxy-octadeca-9,11-dienoate, an unknown compound with an apparent molecular weight of 306, methyl 8-(2',5'-hexylthienyl) octanoate, an unidentified sulfur containing C_{18} ester with an apparent molecular weight of 326, methyl 9,12-epithiostearate, an adduct of methyl *trans,trans*-9,11-octadecadienoate and benzene [bicyclo (4.4.0)-deca-2,5,7-triene-1-(ω-carboxymethyl heptyl)-4 hexyl] and a probable mixture of methyl 9,11-epidithiostearate, methyl 9,12-epidithiostearate, and methyl 10,12-epidithiostearate.

INTRODUCTION

Nucleophilic and radical additions of hydrogen sulfide to nonconjugated methyl esters have been reported previously (1). These studies have been made in the search for extreme pressure additives that can be added to lubricants. Reaction products were separated by preparative gas liquid chromatography (GLC), and identifications were made by nuclear magnetic resonance, mass spectrometry, infrared spectroscopy, and elemental analysis. Among the products identified were mercapto, thio, epithio, and epidithio derivatives of fatty esters. Under ultraviolet radiation hydrogen sulfide adds to olefins in an anti-Markownikoff manner (2). No detailed studies of the mechanism have been made, but it appears that these reactions proceed by a radical chain mechanism. The addition of hydrogen sulfide is a general reaction applicable to terminal, internal, and cyclic olefins. When the double bonds are in a favorable position, dienes react with hydrogen sulfide to yield thiolans and thianes by way of intramolecular addition. Since our last publication (3), we have used GC-MS for identifying the reaction products and extended our studies to include the hydrogen sulfide adducts of methyl *trans,-trans*-9,11-octadecadienoate. High resolution mass spectrometry was used to identify sulfur fragments in the mass spectra.

EXPERIMENTAL

Starting Materials

trans,trans-9,11-Octadecadienoic acid was prepared via a polyester intermediate of ricinelaidic acid by the method of Schneider et al. (4). Pyrolysis of the polyester and simultaneous distillation yielded crude dehydrated acids. Recrystallization from 95% ethanol gave a product which had an absorptivity of 123.7 (methanol) and 114.1 (isooctane) at 231 mμ. Infrared spectroscopy showed absorption at 987 cm^{-1}, a = 1.240 (carbon disulfide). The methyl ester of this product was prepared by a reaction with 2,2-dimethoxypropane in acidic methanol (5).

Hexane was redistilled Skelly B (b.p. 67-70 C) obtained from the Skelly Oil Company. "Thiophene Free" benzene

was "Baker Analyzed" reagent grade which meets ACS specification. The benzene was dried over sodium before use. Hydrogen sulfide was Matheson C.P. grade. 2,2-Dimethoxy propane (98%) was obtained from Dow Chemical Company. Methanol was certified ACS grade from Fisher Scientific Company.

Procedure

Ten g of methyl *trans,trans*-9,11-octadecadienoate was weighed into a three necked reaction tube (12.5 in. x 2.5 in. dia.), and 300 ml of benzene were added. A Teflon-coated magnet was placed in the vessel, and the solution was stirred until all the ester had dissolved. Hydrogen sulfide was introduced through a tube in one of the side necks of the vessel until the solution was completely saturated, and the gas was continually bubbled through the solution at a rate of ca. 2 bubbles per sec during the entire reaction. A quartz center well with a jacketed section for circulating cooling water was introduced in the center neck of the flask, and a Hanovia medium pressure UV lamp (model 8A36) was placed in the quartz well. A reflux condenser was fitted to the third neck of the vessel, and a 25 C bath was placed around the entire apparatus. Samples were removed periodically for GLC analysis.

GC-MS Determinations

Combination GC-MS determinations were obtained with a 6 ft x 1/4 in. 3% JXR column in a Packard model 873 gas chromatograph. The column was interfaced to a Nuclide 12-90-G mass spectrometer through a single stage 1 in. x 1/8 in. rectangular 0.002-in. thick dimethyl silicone membrane enricher. The enricher was maintained at ca. 240 C. The column was programmed from 150 to 250 C at a rate of 4 C/min. Helium was the carrier gas and the flow rate was maintained at 30 cc/min. Data during these determinations were collected by a PDP-8 and were stored and processed on a Modcomp II.

Preparative GLC

Samples separated by GLC were collected in 2-in. No. 14 Teflon tubes inserted at the exit port of a 7620 A Series Hewlett Packard gas chromatograph. Column was 6 ft x 1/4 in. stainless steel packed with 12.5 g of 3% JXR. Program runs were conducted at 180-300 C with a heating rate of 2 C/min and a helium carrier gas flow rate of 30 cc/min. This instrument was fitted with a microsplitter-collector, which provided a 1:10 split ratio (one part to the flame ionization detector and 10 parts to the collector tubes). Samples were rechromatographed to increase purity.

RESULTS AND DISCUSSION

When an internal standard (dodecyl sulfide) is added to the reaction products of hydrogen sulfide and methyl *trans,trans*-9,11-octadecadienoate after 160 hr ultraviolet (UV) radiation in benzene solution at 25 C, approximately one-half of the product is volatile on the GLC; the remainder appears polymeric. In contrast, the products from hydrogen sulfide and methyl linoleate under similar conditions gave over 90% volatile materials. Figure 1 is a mass chromatogram (6) of the product from hydrogen sulfide
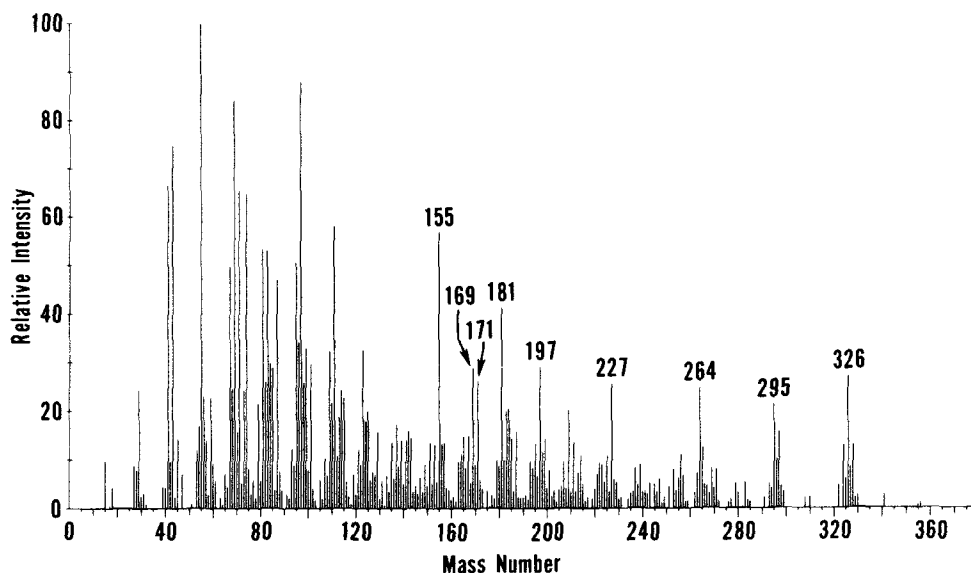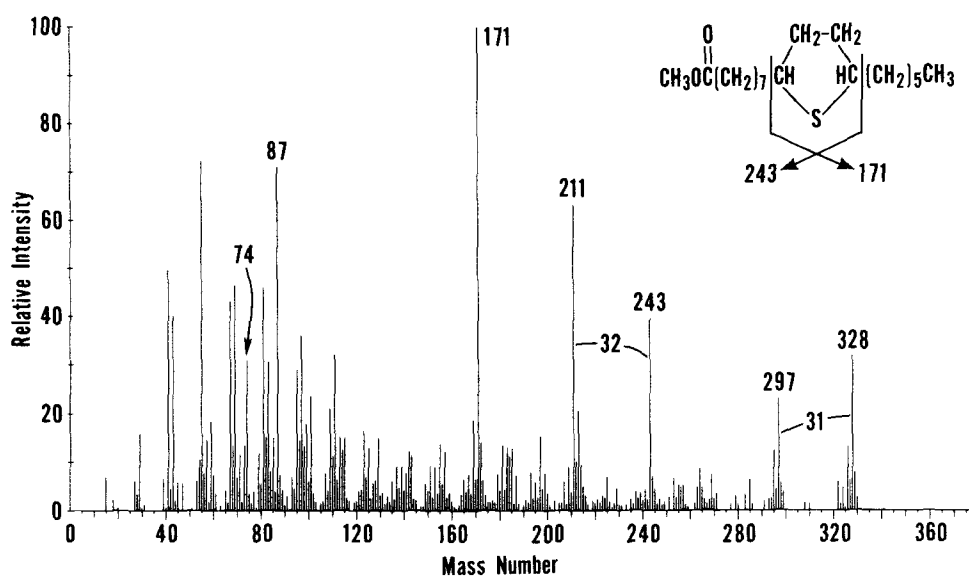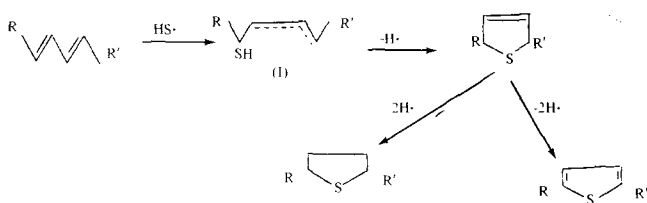
and methyl *trans,trans*-9,11-octadecadienoate after 160 hr UV radiation in benzene at 25 C. Peak A is composed primarily of methyl oleate with a small amount of methyl stearate, and their presence indicates that hydrogenation-dehydrogenation reactions may occur along with addition of hydrogen sulfide. When analyzed on an EGSS-X, column peaks A and B showed presence of methyl stearate, methyl oleate, and geometric isomers of methyl 9,11-octadecadienoate. Peak A[1] (shoulder at start of peak B) has a mass spectrum similar to that reported for methyl 9,12-epoxy-octadeca-9,11-dienoate (7). Peak C is tentatively identified as an oxygenated fatty ester. Peaks A[1] and C may have originated by a reaction of methyl *trans,trans*-9,11-octa-decadienoate with air that could have entered the reaction during sampling.

A preparative GLC sample of peak D (Fig. 1) was collected and a mass spectrum obtained. Figure 2 shows the spectrum with underlined molecular formulas obtained by high resolution mass spectrum peak matching. These peaks were determined to 1 millimass, and sulfur was detected in all of the principal fragment ions (324, 253, and 181). These data are consistent for methyl 8-(2',5'-hexylthienyl)-octanoate. The intense fragment 181 and its companion fragment 253 is accountable by ring expansion of the thenyl derivative to thiopyrilium ions:

Similar expansion are reported for thenyl ions formed by fragmentation of alkylthiophenes (8). Formation of methyl 8-(2',5'-hexylthienyl)octanoate is not easily explainable. Little is known about the detailed steps in the formation of thiophenes. Hartough (9) has a mechanism for the formation of thiophene but a biradical molecule is involved. Ryashentseya et al. (10) investigated the mechanism of thiophene synthesis from n-butane and hydrogen sulfide using [14]C. From radiochromatography data they con-

FIG. 1. Mass chromatogram of H_2S adduct of methyl *trans,-trans*-9,11-octadecadienoate after 160 hr UV radiation in benzene at 25 C.

cluded that the conversion of n-butane into butenes and butadiene does take place during thiophene synthesis. These authors indicate that this stepwise dehydrogenation is not the only possible route for thiophene formation. They do not present a mechanism for the formation of thiophene from butadiene but only suggest a dehydrogenation step. Our studies on the addition of hydrogen sulfide to methyl *trans,trans*-9,11-octadecadienoate indicate that dehydrogenation probably occurs. A likely mechanism for the overall reaction is:

FIG. 2. Mass spectrum of preparative gas liquid chromatographic sample of peak D (Fig. 1) with underlined chemical formulas obtained by high resolution peak matching.

FIG. 3. Mass spectrum of peak E (Fig. 1).

FIG. 4. Mass spectrum of methyl 9,12-epithiostearate (peak F, Fig. 1).

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R and R' are CH₃OC(CH₂)₇ and CH₃(CH₂)₅

These reactions may occur through triplet states available by photochemical excitation (11). Triplet states are important intermediates in organic chemistry and lead to products which can be rationalized as arising via the formation of the most stable diradical intermediate. Since the reaction was run in benzene (a high energy sensitizer), it is likely that the reaction is a triplet state reaction in which the diene is sensitized to give the radical (I) proposed in the mechanism.

Formation of thiophene derivatives from hydrogen sul-

fide and unsaturated fatty esters is not confined to fats with conjugated dienes. When a mass chromatogram was obtained on the reaction product of hydrogen sulfide and methyl linoleate under UV radiation in benzene solution at 25 C, small amounts of thiophene derivatives were also detected.

Figure 3 is the mass spectrum of peak E which appears to be an unknown with an apparent molecular weight of 326. Unfortunately this peak is not completely separated from methyl 8-(2',5'-hexylthienyl)octanoate and methyl 9,12-epithiostearate, and interpretation of the mass spectrum is difficult. Fragment ions at 326, 295, 227, 183, 169, and 155 are not characteristic of the two contaminants. These fragment ions suggest groups or rings at the 8, 9, 10, 11, 12, and 13 positions. This product could be a mixture of unsaturated mercapto compounds and/or cyclic sulfides. Attempts are in progress to separate this product from methyl 8-(2,'5'-hexylthienyl)octanoate and methyl 9,12-epithiostearate.

The mass spectrum of peak F is shown in Figure 4, and this spectrum is consistent for that of methyl 9,12-epithiostearate (12). This compound is the result of intramolecular
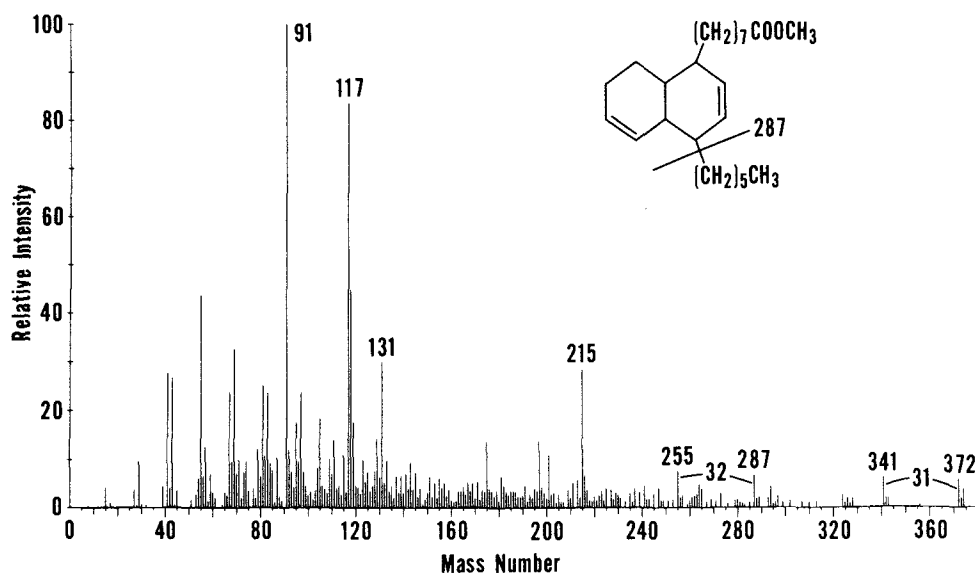
FIG. 5. Mass spectrum of bicyclo (4.4.0) deca-2,5,7-triene, 1-(ω-carboxymethylheptyl), 4-hexyl (peak G, Fig. 1).
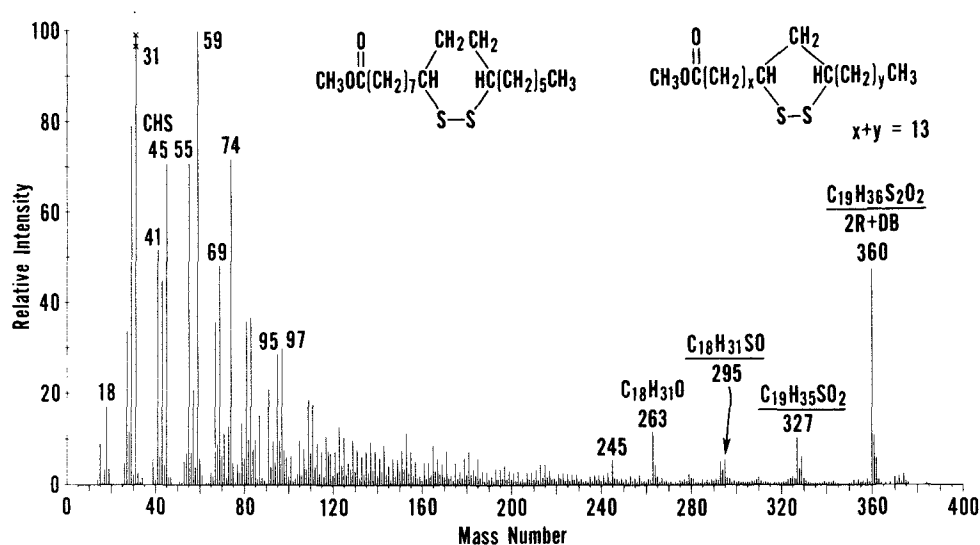

FIG. 6. Mass spectrum of peak H (Fig. 1).

addition of either or both methyl 9-mercapto-octadec-11-enoate and methyl 12-mercapto-octadec-9-enoate.

Figure 5 is the mass spectrum of peak G (Fig. 1). The spectrum is consistent for bicyclo (4.4.0) deca-2,5,7-triene-1-(ω-carboxymethyl heptyl) 4-hexyl, and we are tentatively indicating it as such. It has a parent peak of 372 with a fragment ion at 341 (loss of methoxy), a fragment ion at 287 accountable by:
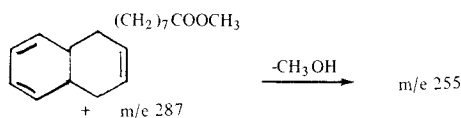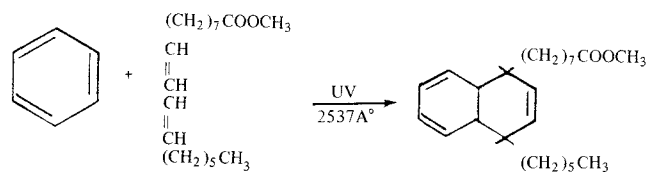

and a fragment ion at 215 accountable by:
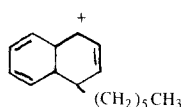
Fragment ions at 91, 117, and 131 are attributed to the breakdown of:
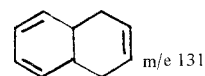
Cavalli et al. (13) report similar fragments on the mass spectra of related compounds. The photochemical reaction between benzene and methyl trans,trans-9,11-octa-decadienoate is probably a Diels Alder type reaction:

Benzene under usual reaction conditions is considered an inert solvent because of its high resonance energy ($\cong 36$ k cal/mole). This energy is not a barrier to photo-chemical reactions with UV radiation at 2537A° ($\cong 115$ k cal/mole) where benzene absorps UV. Photoadditions of olefins to benzene have recently become well known (14), and Wilzbach et al. (15) rule out that olefin additions pro-

ceed through a benzvalene intermediate.

The mass spectrum of peak H is shown in Figure 6. This spectrum is similar to the spectrum of one of the products obtained from the addition of hydrogen sulfide to methyl linoleate (16). It is a stable compound as evidenced by a high intensity parent mass of 360. Other prominent fragment ions show loss of -SH (327), loss of methanol (295), and loss of a second sulfur atom (263). The 263 contains no sulfur since there is no evidence for S_{34} at mass 265. This product is probably a mixture of methyl 9,11-epidithiostearate, methyl 9,12-epidithiostearate, and methyl 10,12-epidithiostearate.

ACKNOWLEDGMENT

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