

Letter

Natural sulphurization of ketones and aldehydes: A key reaction in the formation of organic sulphur compounds

STEFAN SCHOUTEN, GIEL B. VAN DRIEL, JAAP S. SINNINGHE DAMSTÉ, and JAN W. DE LEEUW
Division of Marine Biogeochemistry, Netherlands Institute of Sea Research (NIOZ), PO Box 59,
1790 AB Den Burg, Texel, The Netherlands

(Received August 19, 1993; accepted in revised form October 21, 1993)

Abstract—Acids, ketones, aldehydes, and alcohols were tested in the laboratory as substrates for hydro-sulphurization under mild conditions. Ketone and aldehyde model compounds (i.e., 2-nonanone, nonanal, cholestan-3-one and phytanal) formed significant amounts of organic sulphur compounds, in which the oxo group was substituted by a polysulphide moiety. These results are used to explain the formation of several organic sulphur compounds reported in immature S-rich sediments.

INTRODUCTION

SULPHUR INCORPORATION INTO organic matter in the sub-surface occurs during very early diagenesis (e.g., SINNINGHE DAMSTÉ et al., 1989; KOHNEN et al., 1990b). Hydrogen sulphide (SINNINGHE DAMSTÉ et al., 1989; FUKUSHIMA et al., 1992), polysulphides (KOHNE et al., 1989), and elemental S (SCHMID, 1986; ROWLAND et al., 1993) have been suggested as the inorganic S species which react with lipids. Recently the addition of hydrogenpolysulphide ions to isolated double bonds under mild conditions was simulated in the laboratory (DE GRAAF et al., 1992). This resulted in formation of low- and high-molecular-weight organic S compounds (OSC) from geochemically relevant model compounds such as phytanes and phytol. The type of products generated by this reaction are similar to those found in immature S-rich sediments. Therefore, sulphurization is relatively fast and can occur under conditions similar to those in anoxic water columns and surface sediments.

Many lipids in the water column and sediments have oxygen functionalities such as acids, aldehydes, ketones, and alcohols. Whether these oxygenated lipids can react with hydrogenpolysulphides under the mild sedimentary conditions is not known, but is important because the sulphurized counterparts of compounds will be better preserved and their (partial) absence as such may bias the sedimentary record against these compounds. For instance, an important geochemical parameter for determining the temperature of surface waters in ancient oceans is the U_{37}^K index (BRASSELL et al., 1986). This parameter is based on the distribution of unsaturated C_{37} methylketones, a parameter related to surface water temperatures. It has already been suggested that these compounds can react with S (SINNINGHE DAMSTÉ et al., 1988) since in particular sediments (e.g., Jordanian Oil Shale) relatively high amounts of S-bound C_{37} - C_{39} *n*-alkyl-moieties are present. This would imply the reaction of the oxo-group during natural sulphurization and might result in a change of the distribution patterns of the remaining ketones.

Here we report the results of laboratory simulation experiments on model compounds with an oxygen functionality. These results may explain the mechanism of formation of several types of organic S compounds occurring ubiquitously in immature S-rich sediments.

EXPERIMENTAL

Model Compounds

Most of the model compounds used were obtained commercially. 2,6,10,14-tetramethylhexadec-14-enal (phytanal) was synthesized by oxidation of phytol with pyridinium chlorochromate (PARISH et al., 1991).

Sulphurization Reactions

The conditions for the sulphurization experiments were essentially identical to those previously described by DE GRAAF et al. (1992). A two-phase system consisting of water and ethyl acetate was used as reaction medium. Tetrabutyl ammonium bromide was added as a phase transfer agent. NaSH and S_8 and the substrate were mixed in a 100:5:1 molar ratio. The reaction time was typically one week, and the temperature of the reaction vessel was maintained at 50°C.

The selective cleavage of S-S bonds with methyl lithium (MeLi) and methyl iodide (MeI) has been described previously (DE GRAAF et al., 1992).

Gas Chromatography (GC)

GC was performed using a Carlo Erba 5300 instrument, equipped with an on-column injector. A fused silica capillary column (25 m × 0.32 mm) coated with CP Sil-5 (film thickness 0.12 μm) was used with He as carrier gas. For detection, a flame ionization detector (FID) was used. The samples (dissolved in ethyl acetate) were injected at 70°C; the oven was then programmed at 10°C/min to 320°C and held isothermal for 10 min.

Gas Chromatography–Mass Spectrometry (GC–MS)

GC–MS was performed on a Hewlett-Packard 5480 gas chromatograph interfaced to a VG-70S mass spectrometer operated at 70 eV with a mass range of m/z 40–800 (resolution 1000; cycle time 1.8 s). The gas chromatograph was equipped with a fused silica capillary column (25 m × 0.32 mm) coated with CP Sil-5 (film thickness

Table 1. Substrates used in sulphurization experiments.

Substrate	Products	Conversion (%)
2-nonanone	polysulphide-linked dimers	10
nonanal	polysulphide-linked dimers	100
5 α -cholest-3-one	polysulphide-linked dimers	85
5 β -cholest-3-one	polysulphide-linked dimers	99
phytenal	cyclic di- and trisulphide	100
dodecanoic acid	none	0
2-nonanol	none	0

= 0.2 μ m). The carrier gas was He. The samples were injected on-column at 50°C, and subsequently the oven was programmed to 300°C at 10°C/min at which it was held for 10 min.

RESULTS OF MODEL EXPERIMENTS

To investigate the reactivity of alcohols and acids, two substrates were used in the sulphurization reaction (Table 1). None of these reacted. However, when ketones and aldehydes were used as substrates, the reaction mixture always contained significant amounts of products. The distribution

pattern of the reaction products depended on the position of the oxo group in the reactant carbon skeleton.

In the case of 2-nonanone, several S compounds were identified (Fig. 1) and all result from a selective substitution of the oxo group by S. The S compounds possessing a butyl group are formed as side products through reaction with the phase transfer reagent used (tetrabutyl ammonium bromide). Treatment of the reaction product mixture with MeLi/MeI, a reagent which selectively cleaves S-S bonds (KOHENEN et al., 1991), yielded 2-(methylthio)-nonane as the only S compound thus demonstrating the selective substitution. In the case of an aldehyde, nonanal, the same reaction pathway can be inferred. The oxo group was substituted by S, as demonstrated by the MeLi/MeI treatment of the reaction product mixture yielding only 1-(methylthio)-nonane.

Another geochemically relevant model compound used as substrate was 5 α -cholestan-3-one. GC analysis of the reaction products revealed an unresolved complex mixture in addition to the starting compound. GC-MS analysis of the products released by MeLi/MeI treatment revealed two dominant S compounds (Fig. 2). Based on previously published mass spectra and retention times (KOHENEN et al., 1993), these were identified as 3 α -(methylthio)-5 α -cholestane and 3 β -

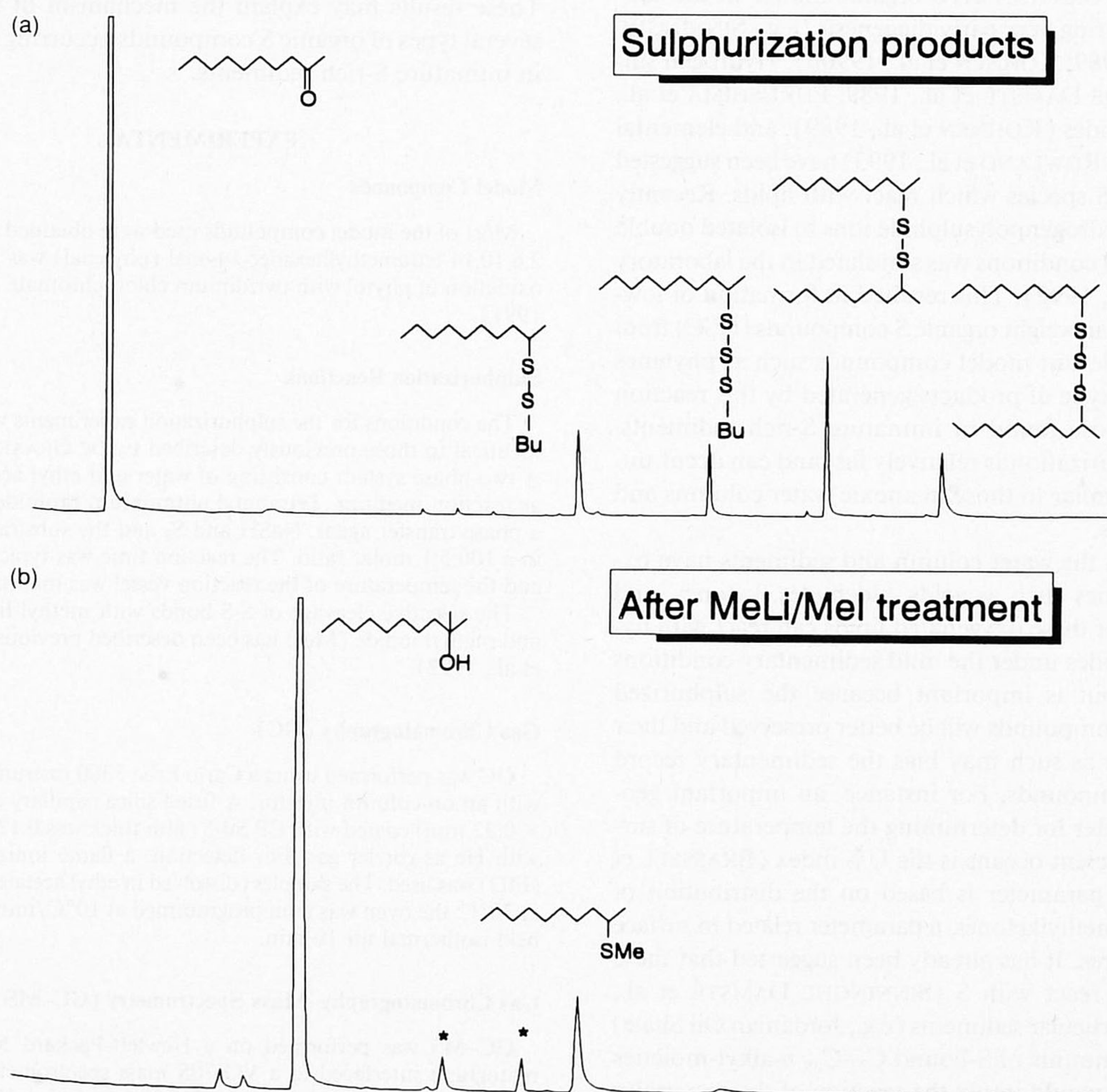


FIG. 1. (a) FID-trace of reaction mixture after sulphurization of 2-nonanone. (b) Gas chromatogram of MeLi/MeI products. Bu = butyl, * = contamination.

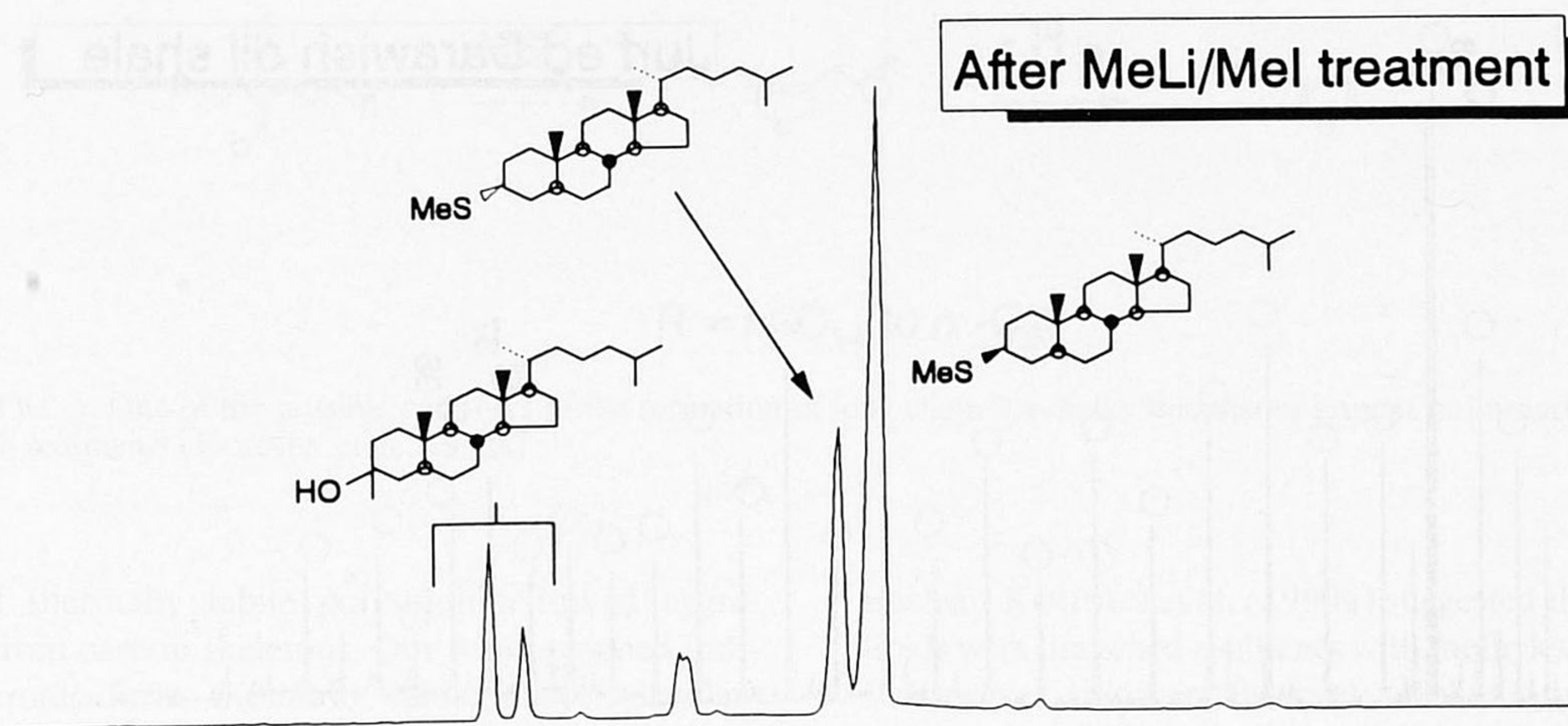


FIG. 2. Gas chromatogram of products released after MeLi/MeI treatment of reaction mixture after sulphurization of 5 α -cholest-3-one.

(methylthio)-5 α -cholestane. The isomers were present in a 2:1 ratio (3 β :3 α), indicating the preferential attachment of S in an equatorial position. In the case of 5 β -cholestan-3-one a similar reaction occurred. The ratio between 3 α and 3 β substituted cholestanone was, however, different, and the 3 α -isomer was now much more abundant (3 β :3 α = 1:7). In this case the axial position was energetically more favourable. The reaction of polysulphides with cholestanones thus leads to the formation of thermolabile dimers where the steroids are connected via a polysulphide bridge attached to the C-3 positions.

Phytenal is a ubiquitous compound in Recent sediments and is thought to be formed by oxidation of phytol (RONTANI et al., 1990). Laboratory hydrogensulphurization of phytenal produced only two S compounds in high yield (Fig. 3; Table 1). Both result from intramolecular incorporation of S. The product distribution is similar to that previously observed when phytol was used as a substrate (DE GRAAF et al., 1992). In this case, however, the yields were much higher; phytenal could not be detected in the reaction mixture, indicating a complete conversion to S compounds.

The model experiments demonstrate that alcohols and acids are not reactive towards the hydrogenpolysulphide ions. Ketones and aldehydes, however, do seem to be very reactive and form unique S compounds. To the best of our knowledge, hydrosulphurization of ketones and aldehydes under these conditions has not been reported previously.

GEOCHEMICAL IMPLICATIONS

Several previously reported compound distributions in immature S-rich sediments can now be explained by invoking natural sulphurization of ketones or aldehydes. For instance, KOHNEN et al. (1991, 1993) and ADAM et al. (1991, 1992) reported that S is preferentially linked to C-3 in S-bound steroid moieties. Since alcohols seem to be nonreactive, as indicated by the model experiments, these compounds are probably derived mainly from 3-ketosteroids which occur ubiquitously in Recent sediments (MERMOUD et al., 1984). Furthermore, S-bound dinosterane is reported to be linked only at C-3 (KOHNEN et al., 1991), an observation which cannot be explained by S addition to a diagenetically formed

Sulphurization of phytenal

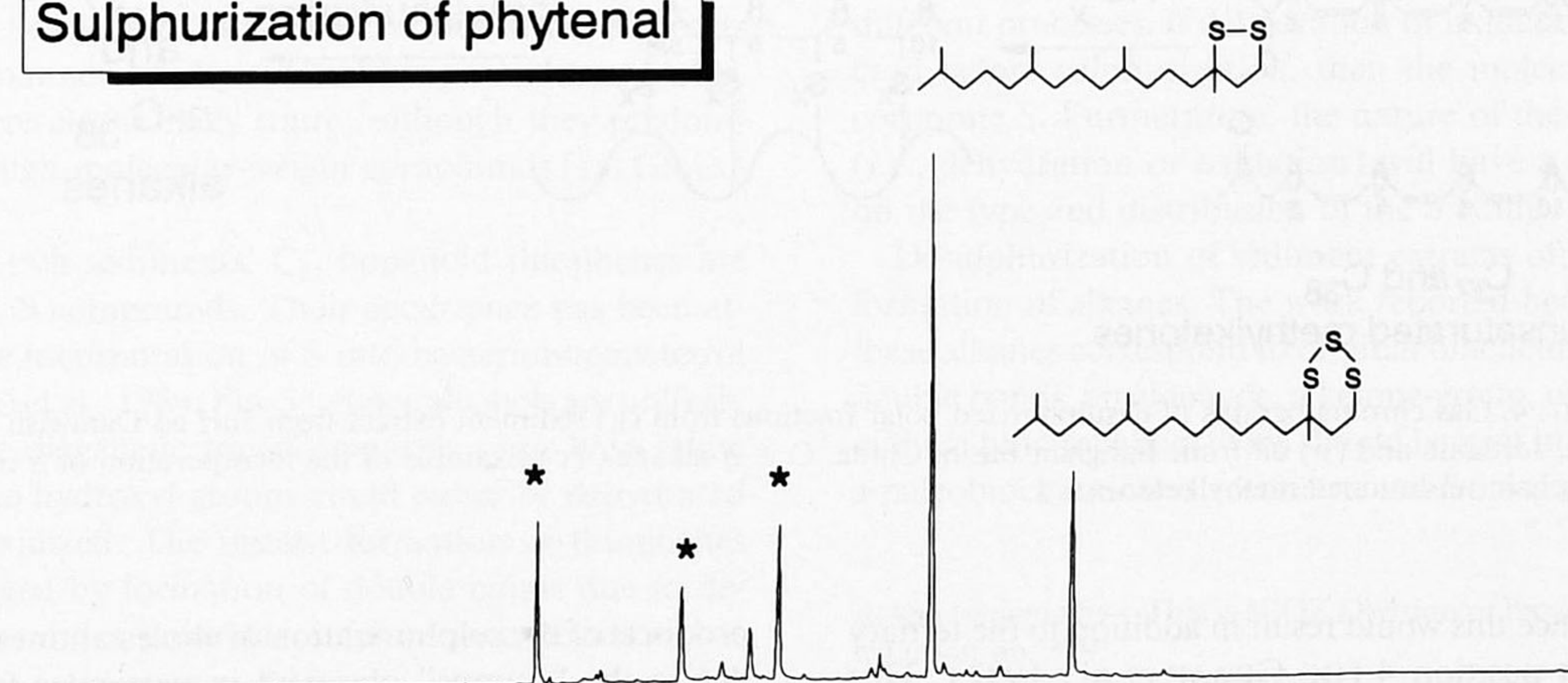


FIG. 3. Gas chromatogram of products present in reaction mixture of sulphurization of phytenal. Stars indicate side products generated during the synthesis of phytenal.

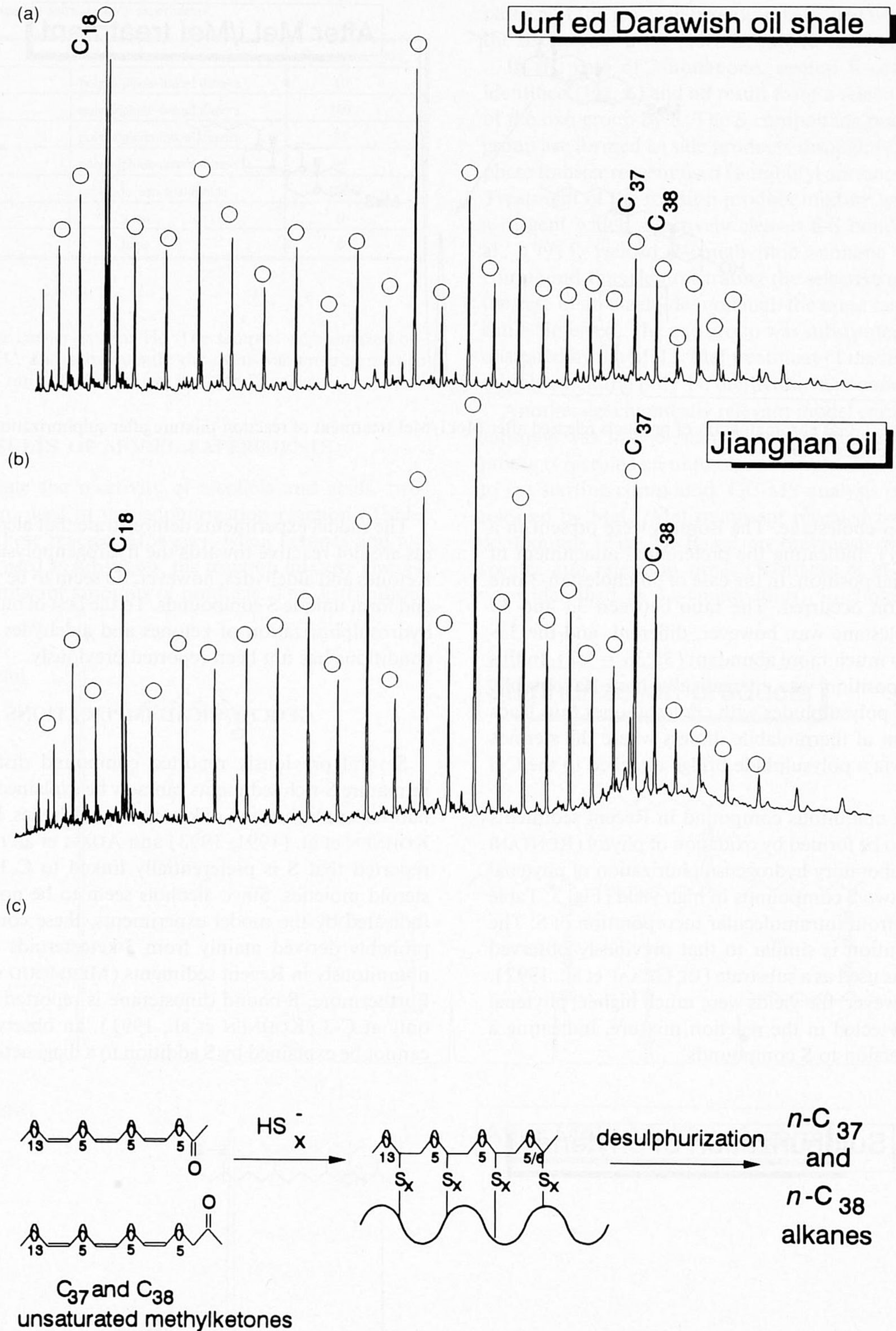


FIG. 4. Gas chromatograms of desulphurized polar fractions from (a) sediment extract from Jurf ed Darawish oil shale, Jordania and (b) oil from Jiangnan Basin, China. ○ = *n*-alkanes. (c) Example of the incorporation of S into long-chain unsaturated methylketones.

double bond, since this would result in addition to the tertiary carbon-atom at position 4 (DE GRAAF et al., 1992). This strongly indicates that dinosterone was the original lipid which reacted with S. The “humps” in the GC-traces of the reaction

products of the sulphurization of cholestanones are very similar to the “humps” observed in particular fractions from immature S-rich sediment extracts (KOHENEN et al., 1991). The authors suggested that these “humps” are primarily

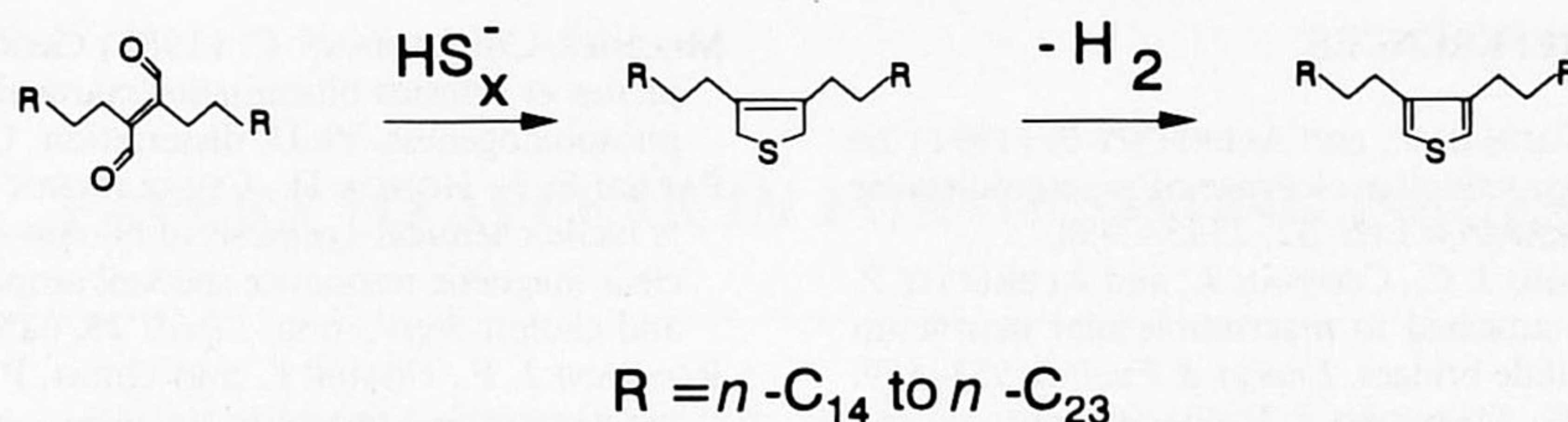


FIG. 5. One of the possible pathways of the formation of long chain 3,4-dialkylthiophenes present in immature S-rich sediments (KOHNE et al., 1990a).

composed of thermally labile polysulphide-linked aggregates with steroid carbon skeletons. Our results indeed indicate that steroids form thermally labile high-molecular-weight OSC.

In some S-rich sediments and oils there is a predominance of S-bound C_{37} and C_{38} *n*-alkanes (e.g., SINNINGHE DAMSTÉ et al., 1988; MEUNIER-CHRISTMANN, 1988; RULLKÖTTER and MICHAELIS, 1990). For instance, desulphurization of polar fractions of a Jordanian oil shale extract (SINNINGHE DAMSTÉ et al., 1988) and of an oil from China (SINNINGHE DAMSTÉ et al., 1989) clearly show an increased abundance of C_{37} and C_{38} *n*-alkanes (Fig. 4). These compounds are probably derived from C_{37} and C_{38} unsaturated methyl and ethylketones biosynthesized by certain coccolithophorid algae (VOLKMAN et al., 1980). Since the keto-group will react as well as the double bonds with inorganic S species, OSC are formed which are liberated as C_{37} and C_{38} *n*-alkanes upon desulphurization. This implies that the use of these ketones as paleotemperature indicators (BRASSELL et al., 1986) may be restricted to S-poor sediments, since sulphurization of these compounds may lead to their absence in S-rich sediment. Recent experiments have shown that ketones react faster than mid-chain double bonds (SCHOUTEN et al., 1993) indicating that partial sulphurization of diunsaturated and triunsaturated methylketones does not necessarily changes the U_{37}^K index significantly, though care has still to be taken.

The predominance of the dithiolane and trithiane isomers with a phytane carbon skeleton in the Vena Del Gesso and Peru upwelling area sediments (KOHNE et al., 1989) may reflect S incorporation into phytenal. This will exclusively yield low-molecular-weight C_{20} isoprenoid polysulphides. Phytol cannot be excluded as a source, however, since it reacts in a similar manner as phytenal, although in lower yields. Phytadienes are also a likely source although they predominantly yield high-molecular-weight compounds (DE GRAAF et al., 1992).

In many S-rich sediments, C_{35} hopanoid thiophenes are major organic S compounds. Their occurrence has been attributed to the incorporation of S into bacteriohopanetetrol (VALISOLALAO et al., 1984; Fig. 5). Since alcohols are unlikely to react, some diagenetic transformations must have taken place first. The hydroxyl groups could either be dehydrated or partially oxidized. The instant formation of thiophenes can be envisaged by formation of double bonds due to dehydration after intramolecular sulphur incorporation has taken place.

The long-chain C_{36} - C_{54} 3,4-dialkylthiophenes are another group of thiophenes whose mechanism of formation has been

unclear. KOHNE et al. (1990a) suggested that the precursor lipids were branched *n*-alkenes with methylenic double bonds. If, however, this were the case, sulphur would have reacted preferentially at the tertiary carbon atom (DE GRAAF et al., 1992) resulting in macromolecularly bound carbon skeletons which have not been observed. An alternative formation pathway can be suggested starting from an unsaturated dialdehyde (Fig. 5). Reaction of polysulphides with these, until now hypothetical, lipids would instantly form the thiophene and not lead to any macromolecularly bound dimethyl-branched alkanes or 3,4-dialkylthiolanes. WAKEHAM et al. (1993) invoked a somewhat similar transformation for Black Sea sediments to explain the early diagenetic formation of a C_{28} thiophene. The same hypothesis may explain the formation of specific highly branched isoprenoid (HBI) thiophenes identified in some sediments (SINNINGHE DAMSTÉ and RIJSTRA, 1993). Instead of the suggested formation via the anti-Markovnikov addition of S to HBI carbon skeletons containing methylenic double bonds, a formation from unsaturated HBI aldehydes would lead to the reported HBI thiolane and thiophene isomers. Unsaturated HBI ketones have been tentatively identified recently in sediments (DE LAS HERAS, 1991).

The laboratory experiments and geochemical data suggest that in general alcohols may become sulphurized only if they previously undergo some form of diagenetic transformation. The hydroxyl group can dehydrate, forming a double bond suitable for reaction with inorganic S species. The alternative is oxidation of the hydroxyl group to an oxo group which can react with hydrogen polysulphides. Whether an alcohol will become sulphurized may depend on the timing of the different processes. If dehydration or oxidation does not proceed before sulphurization, then the molecule will not incorporate S. Furthermore, the nature of the transformation (i.e., dehydration or oxidation) will have a profound effect on the type and distribution of the S compounds formed.

Desulphurization of sediment extracts often result in the formation of alkanes. The work reported here indicates that these alkanes correspond to original biochemicals containing double bonds, an aldehyde, a ketone-group, or a combination of these functionalities. This should be kept in mind whenever a paleobiochemical is reconstructed from a particular OSC.

Acknowledgments—This is NIOZ Division of Biogeochemistry Contribution no. 319.

Editorial handling: G. Faure

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