

Low-temperature addition of hydrogen polysulfides to olefins: formation of 2,2'-dialkyl polysulfides from alk-1-enes and cyclic (poly)sulfides and polymeric organic sulfur compounds from α,ω -dienes †

Wim de Graaf,^{*,a,b} Jaap S. Sinninghe Damsté^{a,c} and Jan W. de Leeuw^{a,c}

^a Organic Geochemistry Unit, Faculty of Chemical Engineering and Materials Science, Delft University of Technology, De Vries van Heystplantsoen 2, 2628 RZ Delft, The Netherlands

^b Centre for Limnology, Netherlands Institute of Ecology, Rijksstraatweg 6, 3631 AC Nieuwersluis, The Netherlands

^c Division of Marine Biogeochemistry, Netherlands Institute for Sea Research (NIOZ), PO Box 59, 1790 AB Den Burg, Texel, The Netherlands

Hydrogenpolysulfide ions, generated by the reaction of hydrosulfide ions and elemental sulfur, react in a polar organic solvent with alk-1-enes and alka- α,ω -dienes under very mild conditions: 20–50 °C for 1–10 days. The reagent was prepared either in DMF with Na⁺ as counter-ion (method A) or in EtOAc–H₂O with quaternary ammonium as counter-ion (method B). Hexadec-1-ene yields both by method A and B 2,2'-dihexadecyl polysulfides *via* a Markownikoff-type addition. The overall selectivity of Markownikoff *vs.* anti-Markownikoff addition is *ca.* 35:1. The selectivity decreases at higher temperatures in DMF as solvent probably as the result of a sequence of elimination/readdition reactions. Alka- α,ω -dienes are in a similar way converted (method B) into polymeric polysulfides if the number of methylenes between the double bonds is ≥ 4 . Monomeric cyclic sulfur compounds are obtained if the number of methylenes is < 4 . Penta-1,4-diene yields mainly the cyclic disulfide 3,5-dimethyl-1,2-dithiolane whereas hexa-1,5-diene yields the cyclic monosulfide 2,5-dimethylthiolane as the only product. Hepta-1,6-diene yields cyclic mono- and di-sulfides. Proton-catalysed, simple nucleophilic and radical mechanisms for the 'hydrosulfurization' are excluded. A concerted addition of a hydrogenpolysulfide ion to a double bond is proposed as the actual mechanism. The formation of thiolanes and thianes is explained by the same mechanism operating in an intramolecular fashion.

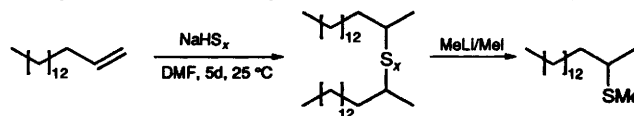
In the course of our studies concerning the formation of organic sulfur compounds in recent sediments, we discovered that sodium hydrogenpolysulfides in an organic solvent react with phytol (3,7,11,15-tetramethylhexadec-2-enol), its dehydrated counterparts, the phytadienes, and even with alk-1-enes at room temperature within a few days.^{1,2} The products obtained from phytadienes are polymeric polysulfides and from alk-1-enes 2,2'-dialkylpolysulfides. The reactions followed Markownikoff's rule, at first sight pointing to a proton-catalysed addition of H₂S_x to a conjugated or isolated double bond. However, to the best of our knowledge, there are no indications from the literature that the reaction of hydrogen(poly)sulfide with isolated double bonds occurs under these mild, near neutral conditions.³ It was reported recently, though, that hydrogenpolysulfides react with conjugated dienes and enones at low temperature.^{4,5}

Here we describe the results from a study focussing on the reaction of hydrogenpolysulfide ions with selected alkenes and alkadienes as substrates under a variety of reaction conditions. Hexadec-1-ene was selected as the substrate for a study of the reactivity depending on the composition of the hydrogenpolysulfide reagent. Subsequently, the reaction was optimized for phase-transfer conditions. Finally, the behaviour of dec-1-ene, dec-5-ene, 2-methylundec-1-ene and α,ω -dienes has been studied. The dienes, with varying methylene-spacing between the double bonds, were selected in order to investigate whether intramolecular pathways are involved in the formation of monomeric cyclic sulfur compounds rather than polymeric polysulfides.

Results

Hydrosulfurization in DMF (method A)

Hexadec-1-ene was allowed to react at room temperature with a ten-fold excess of NaHS_{3,5} in DMF. After 5 days, a mixture of 2,2'-dihexadecylpolysulfides and a trace of hexadecane-2-thiol was formed. Since this product mixture cannot be analysed directly by gas chromatography, because of the thermal instability of the polysulfides, it was treated with MeLi in diethyl ether followed by MeI treatment (Scheme 1). This



Scheme 1 Hydrosulfurization of alk-1-enes and subsequent MeLi–MeI treatment

procedure selectively cleaves polysulfide bridges and transforms them into methylsulfanyl groups.⁶ 2-Methylsulfanylhexadecane was thus obtained in 35% yield. Unchanged hexadec-1-ene was recovered (60%). The structure of 2-methylsulfanylhexadecane was established by ¹H NMR and GC-MS. The ¹H NMR spectrum shows the hydrogen atom at C-2 as a sextet at δ 3.12 and in the mass spectrum the base peak at m/z 75 originates from α -cleavage between C-2 and C-3. Only a trace of 1-methylsulfanylhexadecane was observed by GC-MS (m/z 61; 1:35 as determined by integration of the relevant peaks in the gas chromatogram). The addition thus follows Markownikoff's rule with a high selectivity.

The influence of the overall composition of the hydrogenpolysulfide reagent was studied by the following experiments. Hexadec-1-ene was allowed to react with a ten-fold

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Table 1 Yield of the reaction of hexadec-1-ene with NaHS_x in DMF at 50 °C for 24 h

Stoichiometry	Yield of products (%)	Recovered hexadec-1-ene (%)
NaHS	0	95
NaHS ₂	50	24
NaHS _{3.5}	63	13
NaHS ₆	4	90

excess of NaHS_x ($x = 1, 2, 3.5$ and 6) at 50 °C for 24 h; the yields as function of the overall composition are compiled in Table 1. It should be noted that a solution of NaHS without additional elemental sulfur is insufficient to induce any reaction. A reaction takes place only after addition of elemental sulfur to the solution of NaHS in DMF. The yield of the addition of hexadec-1-ene is good for compositions of NaHS₂ and NaHS_{3.5} but is considerably lower for NaHS₆.

The number of sulfur atoms in the 2,2'-dihexadecyl polysulfides obtained from the reaction of hexadec-1-ene with NaHS₂ and NaHS_{3.5} in DMF at 50 °C was determined by ¹H NMR spectroscopy. From the integrated signals of the H atoms at C-2 and C-2' it was found ‡ that the polysulfide mixture consisted mainly of tri- and tetra-sulfides in a 1:1 ratio independent of the reagent composition. Free thiols were also present with the highest amount (ca. 10%) using NaHS₂ as reagent. Gas chromatographic analyses of the product mixtures confirmed the presence of thiols (10% with NaHS₂ as reagent and only 2% with NaHS_{3.5}).

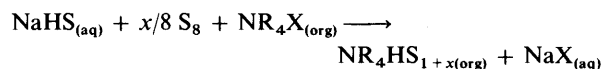
Selectivity and reversibility of the hydrosulfurization. The addition of the hydrogenpolysulfide reagent to hexadec-1-ene in DMF at 50 °C leads to a decrease in the Markownikoff *vs.* anti-Markownikoff selectivity relative to that observed in the reaction at ambient temperature. The selectivity ratio at room temperature was 35:1 but at 50 °C this ratio decreases to 10:1 and becomes even lower at higher temperatures or prolonged reaction times. It is noteworthy that the product mixtures of the 50 °C reaction also contained a small amount of 3-methylsulfanyloctadecane, after MeLi–MeI treatment.

In order to check whether isomerization of initially formed 2,2'-dialkyl polysulfides occurs, octadecane-1-thiol was treated with an excess of NaHS_{3.5} in DMF for 1 d at 75 °C. Octadecane-1-thiol was chosen because it is commercially available in sufficiently pure form (>99%). The products, dioctadecyl polysulfides, were treated with MeLi–MeI and subsequently analysed by GC–MS. Apart from 1-methylsulfanyloctadecane (85%), 2-methylsulfanyloctadecane (9%) and 3-methylsulfanyloctadecane (3%) were found. These findings suggest that under these conditions the hydrosulfurization is to some extent reversible probably due to elimination and readdition reactions with concurrent double-bond isomerization.

Hydrosulfurization in a two-phase system (method B)

The hydrosulfurization can also be performed under mild conditions (50 °C for several days) in a two-phase system consisting of water and ethyl acetate. Hydrogensulfide ions were then extracted from the water phase by a quaternary

ammonium salt. The reactions can easily be performed on a 5 mmol or on a larger scale using readily available chemicals:



Optimal conversions of hexadec-1-ene (up to 95% after 10 d of stirring at 50 °C) were only reached with the use of 2 equiv. of phase transfer reagent§ and 0.5 equiv. of sulfur relative to the substrate. The reaction mixture contained hexadecane-2-thiol (ca. 20% based on GC-analysis), 2,2'-dihexadecyl polysulfides (ca. 70%) and also 2,2'-dihexadecyl monosulfide (5% based on GC analysis). ¹H NMR analysis indicated that the polysulfides consisted of a mixture of di-, tri-, tetra- and higher poly-sulfides. The Markownikoff *vs.* anti-Markownikoff selectivity was 35:1 as determined after treatment of the reaction mixture with MeLi/MeI. The monosulfides were present as two diastereoisomers in a 1:1 ratio and were characterized by the molecular ion at m/z 482 and a major fragment ion at m/z 284 in their mass spectra obtained after GC-MS analysis.

Dec-1-ene, dec-5-ene and 2-methylundec-1-ene

The scope of the hydrosulfurization was further investigated with an alkene with a mid-chain double bond (*trans*-dec-5-ene), an alkene with a tertiary carbon at C-2 (2-methylundec-1-ene) and dec-1-ene as control for the effect of the smaller chain length (Table 2, entries 2–4).

In the case of dec-5-ene most of the starting material was recovered; only small amounts of 5-methylsulfanyloctadecane were obtained after MeLi–MeI treatment of the reaction mixture. The structure of 5-methylsulfanyloctadecane was established by the presence of a major fragment ion at m/z 117 in its mass spectrum.

In the case of 2-methylundec-1-ene the yield (after MeLi–MeI treatment) of 2-methyl-2-methylsulfanylundecane was 58% whilst 40% of the starting material was recovered. The identification of this product is based on a major fragment ion at m/z 89 in its mass spectrum.

Formation of polymeric and heterocyclic sulfur compounds from alka- α,ω -dienes

When alka- α,ω -dienes are used as substrates for the hydrosulfurizations (method B), polymeric or monomeric cyclic sulfur compounds are obtained depending on the methylene-spacing between the double bonds (Table 2; entries 5–10). The long-chain dienes, tetradeca-1,13-diene, deca-1,9-diene and octa-1,7-diene, yielded viscous light-yellow oils indicating their polymeric nature. Treatment of these products with MeLi followed by MeI yielded the corresponding bis-(methylsulfanyl)-alkanes 4–6 as the main monomeric products as shown by GC-MS analysis. The methylsulfanyl groups are mainly bonded to the C-2 and penultimate carbon atoms of the alkyl chain as revealed by the dominant fragment at m/z 75 in their mass spectra. Elemental analysis of the product mixture from deca-1,9-diene indicates an overall molecular formula C₁₀H₂₀S_{2.2}. The ¹H NMR spectrum of these polymers showed that the disulfide linkage is dominant but significant amounts of

‡ The chemical shifts and multiplicities of the H-atoms at C-2 and C-2' recorded at 400 MHz were found to be the most characteristic to unravel the number and distribution of sulfur atoms in the polysulfide linkage. Reference values for ¹H and ¹³C NMR data were obtained from authentic standards synthesized from hexadecane-2-thiol by reaction with I₂, SCl₂ and S₂Cl₂ (see Experimental section; Table 3).

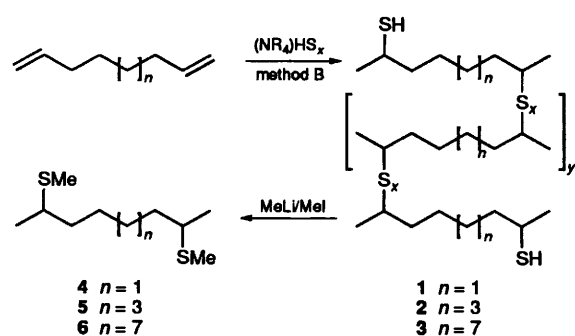
§ The nature of the phase transfer reagent is not so important, but generally they are degraded presumably by a nucleophilic attack on one of the alkyl groups. These alkyl groups are transformed into dialkyl or crossed polysulfides with the product of the addition reaction. Methyl groups from the commercial product, Adogen 464 (methyltri[octyl/decyl]ammonium chloride), are preferably substituted. However, small amounts of octyl and decyl crossed polysulfides are formed and may lead to non-volatile contaminants of the products.

Table 2 Products of the addition of hydrogenpolysulfide ions to alkenes and α,ω -alkadienes

Entry	Substrates	Products
1	Hexadec-1-ene	2,2'-Dihexadecyl polysulfides (A: 80%; B: 65% + 15% hexadecane-2-thiol)
2	Dec-1-ene	2,2'-Didecyl polysulfides (A: 80%; B: 60% + 20% decane-2-thiol)
3	Dec-5-ene	5,5'-Didecyl polysulfides ^a (B: 2%)
4	2-methylundec-1-ene	2,2'-Di(2-methylundecyl) polysulfide ^a (B: 56%)
5	Tetradeca-1,13-diene	1,12-Dimethyldodecamethylene polysulfide polymer 3 (B: 95%)
6	Deca-1,9-diene	1,8-Dimethyloctamethylene polysulfide polymer 2 (B: 90%)
7	Octa-1,7-diene	1,6-Dimethylhexamethylene polysulfide polymer 1 (B: 95%)
8	Hepta-1,6-diene	2,6-Dimethylthiane 11 (B: 35% ^b) + 3,7-Dimethyl-1,2-dithiepane 12 (B: 15% ^b)
9	Hexa-1,5-diene	2,5-Dimethylthiolane 9 (B: 46% ^b)
10	Penta-1,4-diene	3,5-Dimethyl-1,2-dithiolane 7 (B: 40% ^b)

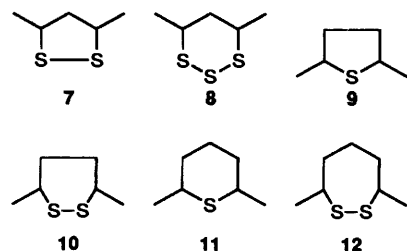
^a Only determined on the basis of MeLi/MeI treatment. ^b Yields of distilled products.

thiol groups (10–40%) are present as well. The presence of residual thiol groups was confirmed by oxidation with iodine resulting in an increase of the viscosity of the product and disappearance of the thiolic smell. From these data we conclude that the compounds formed are the linear polysulfide polymers 1–3 (Scheme 2).



Scheme 2 Hydrosulfurization of alka- α,ω -dienes and subsequent MeLi–MeI treatment

Hepta-1,6-diene and smaller alka- α,ω -dienes yielded volatile monomeric sulfur compounds (Table 2; entries 8–10) upon hydrosulfurization as revealed by GC-MS analysis. The reaction mixtures were distilled at low pressure to isolate the pure monomeric products and facilitate interpretation of the NMR spectra (see Experimental section; Table 4). Penta-1,4-diene yielded 40% of 3,5-dimethyl-1,2-dithiolane 7 together with a small amount of 4,6-dimethyl-1,2,3-trithiane 8. Hexa-1,5-diene yielded, surprisingly, only 2,5-dimethylthiolane 9. No trace of 3,6-dimethyldithiane 10 was detected after distillation. Hepta-1,6-diene yielded both 2,6-dimethylthiane 11 and the cyclic disulfide, 3,7-dimethyl-1,2-dithiepane 12.



Discussion

Nature of the hydrogenpolysulfide reagent

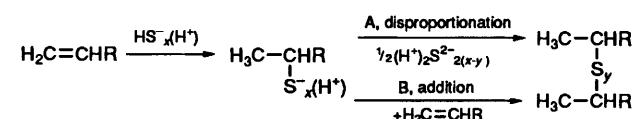
NaHS dissolves in DMF resulting in a clear, almost colourless solution. Elemental sulfur dissolves quickly in a solution of NaHS in DMF and is most probably transformed into

hydrogenpolysulfide anions. Disproportionation of NaHS_x may be expected since it is known that nucleophilic attack on polysulfur chains is fast. There is, however, almost no information available concerning the distribution of species. There are only reports about the composition of Na_2S_x in water and, in that case, disproportionation takes place resulting in S^{2-} and predominantly S_4^{2-} and $\text{S}_{>6}^{2-}$ ions, relatively independent of the stoichiometry of Na_2S_x .⁷

Solutions of NaHS_x in DMF are very dark, varying from blue ($x = 2$) via black ($x = 3$) to red ($x = 6$). The blue colour has been observed previously and was attributed to the presence of radical anions of the type $\text{S}_3^{\cdot-}$.⁸ These radical anions are formed by thermal dissociation of S_6^{2-} anions, a process favoured in aprotic solvents. Disproportionation of NaHS_x not only produces several hydrogenpolysulfide ions but also hydrogen sulfide or higher sulfanes and divalent polysulfide ions which can dissociate further into radical anions. There is, however, no visible evolution of hydrogen sulfide suggesting that this acid-base disproportionation is only small.

The presence of such anionic hydrogenpolysulfides in a rather polar solvent, which is capable of keeping both the reagent and the apolar substrates in solution, appeared important for a good conversion of olefins into sulfur-containing products. For NaHS_x the most suitable solvent is DMF, although for $(\text{NR}_4)\text{HS}_x$, a less polar solvent such as EtOAc is appropriate.

Inter- versus intra-molecular pathways. The most likely process for the formation of dialkyl, polymeric or cyclic polysulfides is a slow addition of hydrogen(poly)sulfide to a double bond, followed by a fast formation of a polysulfide linkage *via* disproportionation or oxidation of the (poly)thiol or (poly)thiolate group (route A; Scheme 3). However, the formation of a polysulfide linkage may also occur *via* an inter- or intra-molecular pathway where the (poly)thiol group adds to a double bond directly in either the same or another molecule (route B). The latter pathway is actually the most likely route to the monosulfides 2,2'-dihexadecyl sulfide, 2,5-dimethylthiolane and 2,6-dimethylthiane; an alternative possibility for the formation of these monosulfides is nucleophilic substitution of a thiolate anion (RS^-) on the α -carbon atom of a dialkyl polysulfide.



Scheme 3 Proposed reaction pathway for the hydrosulfurization

The unlikelihood of proton- or radical-induced additions. The classical view on reactions which follow Markownikoff's rule is that an ionic mechanism is involved. The Markownikoff rule states that the hydrogen atom of a reagent (H-Z) becomes

Table 3 Characteristic ^1H and ^{13}C NMR data for hexadecane-2-thiol and 2,2'-dihexadecyl di-, tri- and tetra-sulfides

Compound	H at C-2	H at C-1	C-1	C-2	C-3
Hexadecane-2-thiol	2.92 heptet	1.33 doublet	25.61	40.96	35.58
2,2'-Dihexadecyl disulfide	2.77 double sextets ^a	1.30 doublet	20.65/20.70	46.67/46.70	36.23
2,2'-Dihexadecyl trisulfide	3.02 sextet	1.36 doublet	20.66	47.18	35.95
2,2'-Dihexadecyl tetrasulfide	3.11 double sextets ^a	1.38 doublet	20.88	47.45	36.18

^a In addition to the expected three band ^1H - ^1H splitting (J 6.6 Hz) there is a further splitting of the signals of the H-atoms at C-2 and C-2' of the di- and tetra-sulfide. This splitting is attributed to the directing influence of the chiral centre at C-2 and C-2' on the axial dissymmetry of the di- and tetra-sulfide linkage. The trisulfide lacks this axial dissymmetry. The values for this splitting are, therefore, given in ppm: 0.007 ppm for the di- and 0.006 ppm for the tetra-sulfide. The splitting is also observed in the ^{13}C NMR spectrum of 2,2'-dihexadecyl disulfide.

Table 4 Selected ^1H and ^{13}C NMR data for cyclic sulfur compounds

Compound name	δ of H at C- α δ of C- α	δ of H at C- β δ of C- β	δ of H at C- γ and C- δ δ of C- γ and C- δ	
<i>trans</i> -3,5-Dimethyl-1,2-dithiolane ^a	1.40 d 20.51	2.09 t 49.72	3.81 sextets 50.28	
<i>cis</i> -3,5-Dimethyl-1,2-dithiolane ^a	1.38 d 20.41	2.66/2.69 t 51.42	3.70 m 51.49	
<i>cis</i> -4,6-Dimethyl-1,2,3-trithiane	1.44 d 26.25	1.68 t 33.98	3.175/3.155 sextets 51.42	
<i>trans</i> -4,6-Dimethyl-1,2,3-trithiane	1.447 d	1.78 t	3.08 m	
<i>trans</i> -2,5-dimethylthiolane ^b	1.33 d 23.65	3.48 m 37.96	2.04/1.70 m 44.50	
<i>cis</i> -2,5-Dimethylthiolane ^b	1.30 d 22.71	3.58 m 39.54	1.53/2.19 m 44.41	
<i>trans</i> -2,5-Dimethylthiane ^c	1.29 d 21.36	2.89 qu of d 33.33	1.91 m 34.73	1.53 m 20.72
<i>cis</i> -2,5-Dimethylthiolane ^c	1.17 d 21.64	2.82 m 38.89	1.65 m 35.94	1.2-1.4 m 27.00
<i>trans</i> -3,6-Dimethyl-1,2-dithiepane ^c	1.25 d 22.36	3.09 m 48.23	1.4-1.9 m 38.22	1.4-1.9 m 24.17
<i>cis</i> -3,6-Dimethyl-1,2-dithiepane ^c	1.24 d 20.90	2.94 m 48.23	1.4-1.9 m 39.06	1.4-1.9 m 21.25

^a The ^{13}C NMR spectrum of the mixture of *cis*- and *trans*-3,5-dimethyl-1,2-dithiolane is in agreement with reported data (M. C. Caserio and J. J. Kim, *Phosphorus, Sulphur and Silicon*, 1985, **23**, 169). The *trans* isomer is obtained in a ratio of ca. 4:1 relative to the *cis* isomer; the *trans* isomer was identified by the deceptively simple triplet at 2.09 ppm in the ^1H NMR spectrum. ^b The ratio of *cis*- and *trans*-2,5-dimethylthiolane was ca. 1:2. ^c Ratios of *cis*- and *trans*-isomers of other products were ca. 1:1.

bonded to the carbon atom of the double bond that already bears the most hydrogens. The mechanistic basis for the rule is that protonation of the double bond generates the most stable carbocation followed by a fast addition of the hetero-substituent (Z^-). The addition of H_2S to, for example, propene, however, needs high temperature ($> 100^\circ\text{C}$) and pressure or strong acid catalysts,³ whilst the current reactions of hydrogen polysulfides with olefinic double bonds proceed at much milder, slightly basic conditions. The likelihood of protonation of a double bond must be effectively zero.

Indications that a simple proton-catalysed mechanism is not operational are also provided by the relative inertness of mid-chain alkenes (*cf.* Table 2, entries 1, 2 and 3). The same reaction rate should be at least expected if a proton-catalysed mechanism is involved. Moreover, 2-methylundec-1-ene, which is the ideal substrate for a proton-catalysed addition, reacts slower than hexadec-1-ene as well (Table 2; entry 4).

At the stoichiometry NaHS_6 at 50°C in DMF the blue colour has almost disappeared and the rate of the hydrosulfurization is also strongly reduced (Table 1), suggesting the involvement of a radical mechanism. Characteristic of a radical mechanism is, however, the formation of anti-Markownikoff products. This is clearly not the case and the possibility that a rearrangement from primary to secondary products occurs after initial addition, is excluded based on the experiment with octane-1-thiol. The involvement of a radical chain mechanism must, therefore, be ruled out.

Proposal for the actual mechanism. The observation that the rate of the hydrosulfurization of alkenes decreases in the

order hexadec-1-ene $>$ 2-methylundec-1-ene $>$ dec-5-ene indicates that the steric accessibility of the alkene is important. The most likely mechanism to be considered is a concerted addition of HS_x^- to a double bond (Fig. 1); a simple nucleophilic addition of HS^- can be excluded, since NaHS alone is unreactive towards hexadec-1-ene. Although polysulfide ions are more thiophylic, we think that the same holds for a direct nucleophilic addition of HS_x^- . More evidence in favour of this view is provided by the reactions with the phytadienes.¹ The product distribution (sulfur atoms mainly at the 2- and 3-positions of the diene system) is in agreement with two times an addition to one of the double bonds rather than a Michael addition which would result in a different product distribution. In the concerted mechanism, the new bonds are formed by a 6-electron rearrangement. Such a process is comparable with the Diels-Alder mechanism and with the Claisen, Cope or MacLafferty rearrangements. Most probably $x = 3$, although species with $x = 2$ or $x > 3$ may be active as well. For that reason, we think that the optimum yield of the reaction is provided by the concentration where most of the polysulfide species will be in the form of HS_3^- (Table 1). The observed Markownikoff selectivity is probably determined by the charge separation of the terminal alkene (hyperconjugation). Molecular mechanics calculations of alk-1-enes using a newly developed force field considering geometry-dependent charges confirms the charge distribution indicated in Fig. 1.⁹

Formation of thiolanes.—The formation of the cyclic mono-sulfides from hexa-1,5-diene and hepta-1,6-diene is noteworthy (Table 2; entries 8 and 9). We believe, however, that

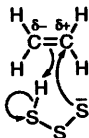


Fig. 1 Concerted addition of HS_x^- to a double bond

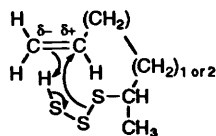
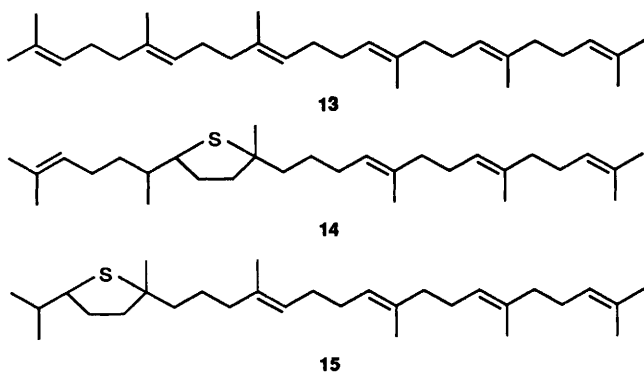


Fig. 2 Formation of cyclic monosulfides

these monosulfides are formed according to a mechanism indicated in Fig. 2. Evidence for this view provided the hydrosulfurization of squalene **13** which resulted in the formation of two thiolanes with structures **14** and **15**.¹⁰ In this case a sulfur moiety introduced at a tertiary position initiates the formation of a thiolane ring through reaction with the secondary carbon atom (instead of the tertiary carbon atom) of the nearest double bond; the Markownikoff rule is, therefore, not obeyed.



The sulfurization of organic matter in marine sediments

Hydrosulfurization proceeds in the presence of a water phase with dissolved hydrogen sulfide ions and resembles natural conditions in the sulfate-reduction zone of a sediment; in most marine sediments the redox potential is controlled by the reversible half-cell: $\text{S}^{2-}(\text{aq}) = \text{S}_0(\text{rhmb.}) + 2\text{e}^-$.¹¹ Deposited lipids come into contact with hydrogen(poly)sulfide-containing pore water. We think that the reaction mechanism described in this paper plays an important role in the incorporation of sulfur into sedimentary organic matter.¹²

Conclusions

- Alk-1-enes react with hydrogen polysulfide ions in polar organic solvents and are converted into 2,2'-dialkyl polysulfides. Nearly quantitative conversions take place at 50 °C after several days.
- Alka- α,ω -dienes are converted into polymeric polysulfides if the methylene-spacing between the double bonds is ≥ 4 . If the methylene-spacing < 4 monomeric cyclic (poly)sulfides are obtained. Cyclic monosulfides are formed only from hexa-1,5-diene and hepta-1,6-diene.
- Proton-catalysed, simple nucleophilic or radical chain mechanisms have to be excluded to explain the current addition reactions.
- Additions are best explained by a 6-electron rearrangement mechanism involving a carbon-carbon double bond and a hydrogen trisulfide ion or a hydrogentrisulfide group.

Experimental

General

NaHS was prepared by the introduction of H_2S (Mattson) in NaOEt, made by the dissolution of sodium in absolute ethanol. Dry NaHS was subsequently precipitated by the addition of dry diethyl ether and filtered off through a sintered glass funnel in an atmosphere of dry nitrogen. It was stored over P_2O_5 in a nitrogen-filled dessicator.¹³ To prevent oxidation of the 'hydrogenpolysulfide' reagent, all reactions were carried out under an atmosphere of dry nitrogen until the work-up procedure. Hydrated NaHS may be used instead of dry NaHS in DMF but the presence of water lowers the solubility of the apolar substrates and as a consequence reduces the yields of the reactions. Hydrated NaSH, hexadec-1-ene, dec-1-ene (purity *ca.* 90% by GC) and alka- α,ω -dienes were obtained from Aldrich.

Hydrosulfurization of alkenes in DMF (method A)

A thermostatted reaction vessel (100 cm³) equipped with a magnetic stirring bar was charged with NaHS (0.56 g, 10 mmol), DMF (25 cm³) and hexadec-1-ene (1.0 mmol) or other substrates; the mixture contained 2 mol% of heptadecane as internal standard. Flowers of sulfur (0, 10, 25 or 50 mmol) were added to the mixture in order to obtain the average compositions NaHS, NaHS₂, NaHS_{3.5} or NaHS₆. After the specified reaction time and temperature the mixture was stirred with a solution of Na₂S₂O₃ (2.5 g) in water (15 cm³). After 30 min the free sulfur had dissolved and the reaction mixture was extracted three times with hexane. The combined extracts were concentrated with a rotary evaporator (with GC analysis) to give a light-yellow oil (0.25 g) in the case of hexadec-1-ene. The product mixture was analysed by GC and ¹H NMR spectroscopy (see text). The remaining reaction mixture was taken up in dry diethyl ether (20 cm³) and a solution of MeLi in diethyl ether (2.0 mol dm⁻³; 1 cm³) was added to it with gentle stirring at room temperature; after 1 min MeI (0.25 cm³) was also added. Stirring was continued for 1 h after which the mixture was carefully hydrolysed with water. The organic layer was separated and the water layer was extracted twice with hexane. The combined organic layer and extracts were dried (MgSO₄) and evaporated under reduced pressure to give a colourless oil (*ca.* 0.20 g, 85–90% recovery) in the case of hexadec-1-ene. The product mixture was analysed by GC, GC-MS and ¹H NMR spectroscopy.

Hydrosulfurization of alkenes mediated by a phase transfer reagent (method B)

A thermostatted reaction vessel (100 cm³) equipped with a magnetic stirring bar was charged with hydrated NaHS (6 g, 0.1 mol), water (10 cm³), tetrabutylammonium bromide (3.22 g, 10 mmol), ethyl acetate (50 cm³), sulfur (0.08 g, 2.5 mmol) and the specified alkene (5 mmol). The reaction mixture was stirred for 10 d at 50 °C after which the contents of the flask were transferred to a separatory funnel. The green-brown organic layer was separated, washed with water and then twice with hydrochloric acid (4 mol dm⁻³; 5 cm³) and then dried (Na₂SO₄) and concentrated on a rotary evaporator to leave light-yellow oily liquids. Cyclic sulfur compounds were distilled at low pressure. The products were analysed by GC, GC-MS and NMR spectroscopy, eventually after MeLi–MeI-treatment (Tables 2 and 4). The product mixture from the reaction of deca-1,9-diene was also subjected to an elemental analysis (Found: C, 56.8; H, 9.2; S, 33.1. Calc. for C₁₀H₂₀S_{2.2}: C, 56.99; H, 9.57; S, 33.43).

Preparation of hexadecane-2-thiol and 2,2'-dihexadecyl di-, tri- and tetra-sulfide

Reduction of dihexadecyl polysulfides with LiAlH₄ following a

known procedure¹⁴ gave hexadecane-2-thiol (95% of the theoretically expected weight). 2,2'-Oxidation of hexadecane-2-thiol with iodine¹⁵ gave dihexadecyl disulfide. Reaction of hexadecane-2-thiol with SCl_2 and S_2Cl_2 , gave tri- and tetrasulfide, respectively.¹⁶ It was observed that use of diethyl ether instead of hydrocarbons gave purer products. After reaction the solvent and HCl were removed by a water pump vacuum. Characteristic NMR data are given in Table 2.

Gas chromatography (GC) and gas chromatography–Mass spectrometry (GC–MS)

GC was performed using a Carlo Erba 5300 instrument equipped with an on-column injector. A fused silica capillary column (25 m \times 0.32 mm) coated with CP Sil-5 (film thickness 0.12 μm) was used with helium as carrier gas. The column effluent was monitored simultaneously by both a flame ionization detector (FID) and a sulfur-selective flame photometric detector (FPD) using a flow-splitter at the end of the column (split ratio 1:2). The samples (dissolved in hexane or ethyl acetate) were injected at 70 °C and the oven was subsequently programmed to rise to 320 °C at a rate of 10 °C min^{-1} ; the oven was held for 5 min at the final temperature.

GC–MS was performed with an HP 5480 gas chromatograph interfaced to a VG-70S mass spectrometer operated at 70 eV with a mass range m/z 40–900 and a cycle time of 1.8 s (resolution 1000). The GC-column and oven program were identical with those described above.

NMR spectroscopy

NMR spectra were recorded on a Bruker 400 MHz spectrometer using pulse Fourier transformation. Shifts (δ) in CDCl_3 are given in ppm relative to tetramethylsilane as external reference. Broadband proton decoupling was applied during the recording of the ^{13}C NMR spectra.

References

- 1 W. de Graaf, J. S. Sinninghe Damsté and J. W. de Leeuw, *Geochim. Cosmochim. Acta*, 1992, **56**, 4321.
- 2 Neth. Patent 92.02072 *Zwaveladditie* (1992).
- 3 W. H. Hoffert and K. Wendtner, *J. Inst. Petr.*, 1949, **35**, 171.
- 4 K. Reinartz, PhD dissertation, University of Köln, 1988.
- 5 E. B. Krein and Z. Aizenshtat, *J. Org. Chem.*, 1993, **58**, 6103.
- 6 M. E. L. Kohnen, J. S. Sinninghe Damsté, A. C. Kock-van Dalen and J. W. de Leeuw, *Geochim. Cosmochim. Acta*, 1991, **55**, 1375.
- 7 (a) E. Muller and J. B. Hyne, *Can. J. Chem.* 1968, **46**, 2341; (b) J. Boulège, C. J. Lord and T. M. Church, *Geochim. Cosmochim. Acta*, 1982, **46**, 453.
- 8 (a) P. Seel, H.-J. Güttler, G. Simon and A. Wieckowski, *Pure Appl. Chem.*, 1977, **49**, 45–54; (b) R. J. H. Clark and D. G. Cobbold, *Inorg. Chem.*, 1978, **17**, 3169.
- 9 A. C. T. van Duin, J. M. A. Baas and B. van de Graaf, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2881.
- 10 S. Schouten, W. de Graaf, J. S. Sinninghe Damsté, G. van Driel and J. W. de Leeuw, *Advances in Organic Geochemistry 1993*, *Org. Geochem.*, 1994, **22**, 825.
- 11 R. A. Berner, *Geochim. Cosmochim. Acta*, 1963, **27**, 563.
- 12 M. E. L. Kohnen, J. S. Sinninghe Damsté, H. L. ten Haven and J. W. de Leeuw, *Nature*, 1989, **341**, 640.
- 13 G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, vol. 1, 1960, p. 325.
- 14 (a) R. C. Arnold, A. P. Lien and R. M. Alm, *J. Am. Chem. Soc.*, 1950, **72**, 731; (b) J. Strating and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 1950, **69**, 638, 909.
- 15 A. Schöberl and A. Eck, *Liebigs Ann. Chem.*, 1936, **522**, 97.
- 16 J. D. Clayton and D. H. Etzler, *J. Am. Chem. Soc.*, 1947, **69**, 974.

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