



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : C07B 45/06, C07C 319/22, C08G 75/14, C07D 335/02, 339/00, 339/04, 337/04, C08J 3/24</p>	AI	<p>(11) International Publication Number: <b>WO 94/12450</b></p> <p>(43) International Publication Date: 9 June 1994 (09.06.94)</p>
<p>(21) International Application Number: PCT/NL93/00254</p> <p>(22) International Filing Date: 29 November 1993 (29.11.93)</p> <p>(30) Priority Data: 9202072 30 November 1992 (30.11.92) NL</p> <p>(71) Applicant (for all designated States except US): TECHNISCHE UNIVERSITEIT DELFT [NL/NL]; Julianalaan 136, NL-2628 BL Delft (NL).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): DE GRAAF, Willem [NL/NL]; Technische Universiteit Delft, Julianalaan 136, NL-2628 BL Delft (NL). DE LEEUW, Jan, Willem [NL/NL]; Technische Universiteit Delft, Julianalaan 136, NL-2628 BL Delft (NL). SINNINGHE, Damsté, Jacobus, Smede [NL/NL]; Technische Universiteit Delft, Julianalaan 136, NL-2628 BL Delft (NL).</p> <p>(74) Agent: SMULDERS, Th., A., H., J.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: METHOD OF PREPARING SULFUR-CONTAINING COMPOUNDS</p>		
<p>(57) Abstract</p> <p>The invention relates to a method of preparing sulfur-containing compounds, comprising reacting a sulfur compound with a compound containing unsaturated carbon-carbon bonds, wherein in a solvent one or more compounds containing non-activated unsaturated carbon-carbon bonds react with monohydrogen polysulfides. The invention further relates to methods of preparing polymeric polysulfides, heterocyclic sulfur compounds and of vulcanizing rubber.</p>		

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Title: Method of preparing sulfur-containing compounds.

The invention relates to a method of preparing sulfur-containing compounds, comprising reacting a sulfur compound with a compound containing unsaturated carbon-carbon bonds, to a method of preparing polymeric polysulfides, to a method of preparing heterocyclic sulfur compounds, and to a method of vulcanizing rubbers.

The addition of sulfur to unsaturated carbon-carbon bonds is a known and widely used reaction in the state of the art.

R.T. Lalonde et al. in *Org. Geochem.* 11 (1987), 563-571 have described that highly activated compounds with unsaturated carbon-carbon bonds undergo a Michael addition in the presence of polysulfide as sulfur donor. These highly activated compounds are generally activated alkenes or alkynes, with an electron acceptor group being attached to one of the unsaturated carbon atoms. More particularly, the publication referred to relates to the Michael addition of conjugated ene carbonyls with polysulfide in alcoholic or aqueous alcoholic solutions. The Michael additions described occur at room temperature.

Further, Vairavamurthy and Mopper in *Nature* 329 (1987), 623-625 have described that the activated compounds described above also undergo a Michael addition when hydrogen sulfide is used. This addition took place under abiotic conditions in seawater.

It has now been found that sulfur can add to non-activated compounds containing an unsaturated carbon-carbon bond, such as alkenes and alkynes, also under very mild conditions. Because of the lack of an activated  $\alpha$ ,  $\beta$ -conjugated system, however, this addition is not a Michael addition as with the known method.

The method of preparing sulfur-containing compounds is characterized, according to the invention, in that in a solvent one or more organic compounds with non-activated

unsaturated carbon-carbon bonds react with monohydrogen polysulfide.

Monohydrogen polysulfide can for instance be obtained by oxidation of monohydrogen monosulfide. In a preferred embodiment, however, monohydrogen polysulfide is formed *in situ* from monohydrogen sulfide in the presence of sulfur.

By the term "non-activated carbon-carbon bond" is meant a compound in which no electron acceptor group is attached to the carbon atoms which are attached to each other through the unsaturated bond referred to. More particularly, no highly electrophilic, electron sequestor groups, such as C=O, -COOH, -COOR and -CN, may be attached to these carbon atoms.

In the present description, "monohydrogen sulfide" is understood to mean a compound of the formula MHS, wherein M is, for instance, an univalent cation, for instance Na<sup>+</sup>, K<sup>+</sup>, a quaternary ammonium ion, etc. Monohydrogen polysulfide can be represented by the formula MHS<sub>x</sub>, wherein M can have the above meanings, while x varies between 2 and 10. Preferably, x varies between 2 and 8, most preferably from 2 to 6. It is not known, incidentally, what (mixture of) monohydrogen polysulfides exactly is formed *in situ* from monohydrogen sulfide and sulfur; it is certain, however, that the reagent does satisfy the formula given.

Without additional steps, dihydrogen (poly)sulfides are not as such suitable for serving as reagent in the method according to the invention. When these compounds are used, the pH of the solutions is reduced too much. Further, no monohydrogen polysulfide is formed *in situ* then, but the equilibrium is on the side of H<sub>2</sub>S and S. However, the use of dihydrogen (poly)sulfides is not excluded, for instance to form a monohydrogen (poly)sulfide in the reaction medium after neutralization by means of a base.

A preferred embodiment of the method according to the invention is characterized in that the reaction is performed at a pH varying between 6 and 10.

The method according to the invention can be carried out under mild conditions. Neither the pressure nor the reaction temperature need to be increased.

Generally, the sulfur addition proceeds very suitably in a solvent at neutral pH and at temperatures varying between  
5 -10°C and 80°C. Preferably, the addition takes place at temperatures between 0°C and 60°C, most preferably between 20°C and 50°C. The pressure in the reaction vessel will as a rule be equal to the outside pressure. In certain cases,  
10 however, increasing or reducing the pressure may give advantages. Catalysts are not requisite. The addition under these mild conditions is as a rule completed between 1 and 10 days, depending on the temperature and the concentration of sulfur donor.

15 It is very surprising that this addition occurs under mild conditions. In fact, heretofore it had only been managed to add sulfur to alkenes or alkynes under considerably less mild conditions.

It is for instance known from an overview article of  
20 Hoffert and Wendtner in the Journal of the Institute of Petroleum 35 (1949), 171, that hydrogen sulfide adds to alkenes only under increased pressure and at temperatures above 150°C utilizing suitable catalysts, for instance strong acids. Further, reference can be made to Jones and  
25 Reid, J.Am.Chem.Soc. 60 (1938) 2452.

In addition, it is known from W.A. Pryor, Mechanisms of Sulfur Reactions (1962) McGraw-Hill, Chapter 5 that a similar reaction of alkenes, alkadienes and allylic alcohols with elemental sulfur to organic sulfur compounds occurs only at  
30 temperatures above 100°C. The reaction products of these reactions typically consist of a nondescript mixture of sulfur containing compounds.

The nature of the solvent is not essential to the practice of the method according to the invention. The sulfur  
35 addition can occur in polar as well as apolar, in protic as well as aprotic solvents. Preferably, however, an organic

solvent or a two-phase solvent system with a phase transfer agent. Optionally, a large excess of the organic unsaturated starting material can be used as solvent.

A preferred embodiment of the method according to the invention is characterized in that an aprotic polar solvent is used. Suitable aprotic solvents are dimethyl sulfoxide (DMSO), hexamethylphosphoric acid triamide (HMPA), N,N-dimethylacetamide (DMA), N-methylpyrrolidone (NMP), tetrahydrofuran (THF) and dimethylformamide (DMF). Most preferably, DMF is used as solvent.

The addition according to the invention can also be carried out in alcoholic solvents, such as isopropanol and butanol. The reaction also occurs in ethanol, albeit much slower than in the aprotic solvents just mentioned.

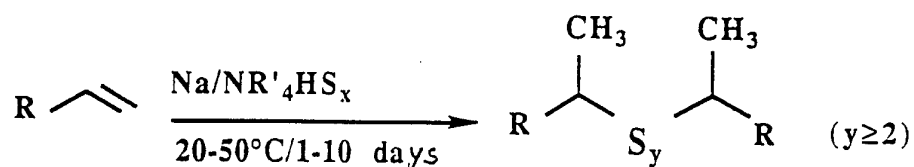
Suitable two-phase systems that can be utilized as medium for the addition according to the invention are mixtures of water with an organic solvent selected from, for instance, ethyl acetate or other esters, such as butyl acetate, isoamyl acetate, diethyl phthalate, acetone or other ketones, such as methylethyl ketone, and toluene. If the addition is carried out in such a two-phase system, typically a phase transfer agent is added. Preferably, this phase transfer agent is a quaternary ammonium salt such as tetrabutylammonium bromide or methyltrioctylammonium chloride. Other phase transfer agents, for instance cholines and polyamines, can also be employed.

The method according to the invention gives the highest yield when it is carried out with exclusion of oxygen. The fact is that oxygen reacts very rapidly with monohydrogen polysulfide.

What product is obtained by the use of the method according to the invention primarily depends on the starting compound which contains at least one unsaturated carbon-carbon bond. In addition, the concentration of this starting compound and of the sulfur donor are of importance. It should be noted that even at a high concentration of sulfur radicals, the addition follows the Markovnikov rule.

When alkenes are reacted with sodium hydrogen sulfide and flowers of sulfur for 1 to 10 days at temperatures between 20 and 50°C, polysulfides are obtained in accordance with the following reaction equation:

5



10

In the final product,  $y$  varies between 2 and  $x$ . Variable  $x$  will as a rule vary between 2 and 10 as mentioned above.

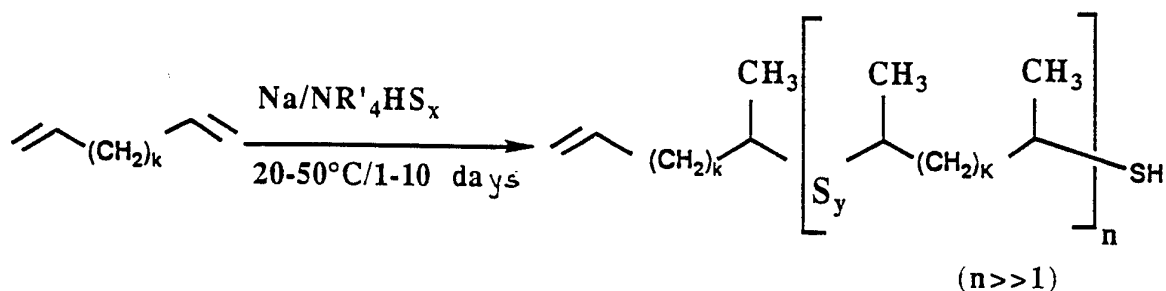
15 When, for instance, 1-decene is started from, then, according to the invention, mainly 2,2'-didecylpolysulfide is obtained.

The mechanism of this reaction is not known. No radical chain reaction occurs, nor can a proton-catalyzed addition occur in view of the neutral pH of the medium. As mentioned above, the addition follows the Markovnikov rule.

In the above-specified reaction equation, an  $\alpha$ -alkene is started from. If the double bond is present at a different position in the molecule, polysulfides with longer side chains are obtained. In this case the reaction typically proceeds slower.

It is also possible to start from alkadienes. Utilizing the method according to the invention, these compounds give polymeric sulfides according to the following reaction equation:

30



Accordingly, the invention also relates to a method of preparing polymeric polysulfides. This method is characterized  
5 in that alkadienes react with monohydrogen polysulfide. Although all alkadienes can be started from, preferably  $\alpha,\omega$ -alkadienes are used.

Polymeric polysulfides possess a major advantage in that they can be broken down relatively rapidly, even in nature.  
10 This (bio)degradability is connected with the presence of many oxidizable and/or reducible polysulfide bridges.

In addition the starting materials are amply available. Further, the properties of the polymeric products can be adjusted very well. It has for instance been found that the  
15 ratio of HS<sup>-</sup>ions to elemental sulfur affects the ratio of free thiol groups and polysulfide bridges. This makes it possible to regulate the degree of polymerization. The free thiol groups that are present in the polymers obtained by the use of the method according to the invention can possibly effect  
20 links between separate polymeric molecules.

If in the method according to the invention alkadienes with a chain of at most 3 carbon atoms between carbon atoms which are attached to another carbon atom through an unsaturated bond, react with monohydrogen polysulfide,  
25 heterocyclic sulfur compounds can be formed. In other words, if the starting material is alkadienes of which a part of the carbon chain can be represented by the formula  $-C=C-(C)_n-C=C-$ , wherein n is at most 3, heterocyclic products can be obtained. Depending on the process conditions and the starting  
30 materials, it is thus possible to form, for instance, thiolanes, thianes and dithiolanes, which can be readily converted, as desired, to unsaturated and aromatic heterocyclic sulfur compounds, such as thiophenes.

Further, it is possible to start from unsaturated  
35 compounds which have been substituted with non-activating groups, such as alkyl groups, hydroxyl groups, etc.



Finally, the invention relates to a method of vulcanizing rubber, which method is characterized in that rubber reacts with monohydrogen polysulfide.

As a rule, in this vulcanization the monohydrogen polysulfide reagent will be contacted with the rubber to be vulcanized in a suitable solvent.

The major advantage of this method is that now a method has been found which enables rubber to be vulcanized under very mild conditions. This enables a better control of the vulcanization process.

The method according to the invention will now be further explained in and by the following examples.

#### Example 1

A thermostated flask with a magnetic agitator was filled with 0.56 g (10 mmol) NaHS, 0.80 g (25 mmol) flowers of sulfur, 0.22 g (1.0 mmol) 1-hexadecene and 25 ml DMF. Then nitrogen gas was blown through until all of the air in and above the solution was replaced with nitrogen. Then the flask was shut off from the air.

Using a magnetic agitator, the contents of this flask were stirred for 24 h at 50°C. Then the contents of the flask were poured into 50 ml of a solution of 2.5 g sodium sulfite in water. In this solution the free sulfur dissolved. Then the reaction products were extracted with hexane. The hexane was subsequently distilled off under reduced pressure.

The product contained 80% 2,2'-dihexadecyl polysulfides, approximately 10% 1-hexadecene and approximately 10% other isomers of hexadecene and hexadecane. The product analysis was carried out with <sup>1</sup>H NMR spectroscopy (Varian VXR 400S (400MHz), CDCl<sub>3</sub>), with gas chromatography (Carlo Erba 5300, capillary silica column 25 m x 0.32 mm, coated with CP-Sil-5, carrier gas helium, injection temperature 70°C, gradient to 130°C at 20°C/min, gradient to 320°C at 4°C/min), and by means of gas chromatography/mass spectrometry (HP 5480 coupled to a VG-70S mass spectrometer, 70 eV, mass range 40-900, cycle time 1.8 s).

From the NMR spectrum it can be derived that the number of sulfur atoms in the polysulfide bridge in the desired product is mainly 3 and 4, whilst a small proportion of the product contains a disulfide bridge.

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#### Example 2

The procedure according to Example 1 was repeated, but instead of 1.0 mmol hexadecene 1.0 mmol of another unsaturated compound was utilized.

10 Starting from 1.0 mmol 1-decene, 80% 2,2'-didecyl polysulfides were obtained.

A mixture of a total of 1.0 mmol *neo*-, *cis*- and *trans*-1,3-phytadiene was stirred at 50°C for 5 days. Upon analysis 60% of the product mixture appeared to consist of isomers of  
15 dithiolanes.

If a similar mixture of 1,3-phytadiene is stirred for 5 days at 20°C instead of 50°C, polymers of phytane units are found to be bonded, with polysulfide bridges formed at the 2,3- and 3,4-positions. The yield of this reaction is 90%.

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#### Example 3

A thermostated flask with a magnetic agitator was filled with 6 g (0.1 mol) NaHS.aq, 0.16 g (5 mmol) flowers of sulfur, 2.24 g (10 mmol) 1-hexadecene, -6.22 g (20 mmol)  
25 tetrabutylammonium bromide, 50 ml ethyl acetate and 10 ml water. Air is again replaced with nitrogen. Then stirring was done at 50°C for 10 days.

After completion of the reaction, the organic layer was separated from the aqueous layer. This organic layer was  
30 washed with water and then with diluted hydrochloric acid. Then the solvent, the ethyl acetate, was distilled off under reduced pressure.

The product contained 65% 2,2'-dihexadecyl polysulfides, and 15% 2-hexadecane thiol.

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#### Example 4

The procedure according to Example 3 was repeated, but instead of 10 mmol hexadecene 10 mmol of a different unsaturated compound was used.

Starting from 10 mmol 1-decene, 60% 2,2'-didecyl  
5 polysulfides and 20% 2-decane thiol were found, whilst 10 mmol 1,13-tetradecadiene yielded 95% of a 1,12-dimethyl-dodecamethylene polysulfide polymeric mixture.

A 1,8-dimethyloctamethylene polysulfide polymeric mixture was obtained in a yield of 90%, starting from 1,9-decadiene.  
10 An element analysis was performed on the polymeric mixture obtained and the result found was  $C_{10}H_{20}S_{2,2}$ .

A reaction mixture containing 1,7-octadiene gave a high yield (95%) of 1,6-dimethylhexamethylene polysulfide polymer, whilst in addition 3% 2,7-dimethyl thiepan was found.

15 Shorter dienes yielded mainly small compounds in the reaction mixture according to this example. From 1,6-heptadiene, after distillation, 35% 2,6-dimethyl thiane and 15% 3,7-dimethyl-1,2-dithiepan were obtained. 1,5-hexadiene yielded 46% 2,5-dimethyl thiolane, whilst from 1,4-pentadiene  
20 40% 3,5-dimethyl-1,2-dithiolane was formed.

A mixture of a total of 10 mmol *neo*-, *cis*- and *trans*-1,3-phytadiene was stirred for 5 days at 20°C instead of 50°C. The product comprised 90% polymers of phytane units, with polysulfide bridges formed on the 2,3- and 3,4-positions.

25 A reaction mixture in which acetylphytol constituted the unsaturated starting material was stirred at a temperature of 50°C for 4 weeks. This compound yielded 38% 3-methyl-3-(4,8,12-trimethyltridecyl)-1,2-dithiolane.

CLAIMS

1. A method of preparing sulfur-containing compounds, in which a sulfur compound reacts with a compound containing unsaturated carbon-carbon bonds, characterized in that in a solvent one or more organic compounds with non-activated  
5 unsaturated carbon-carbon bonds react with monohydrogen polysulfide.
2. A method according to claim 1, characterized in that monohydrogen polysulfide is formed *in situ* from monohydrogen sulfide in the presence of sulfur.
- 10 3. A method according to claim 1 or 2, characterized in that the reaction is carried out at a pH varying between 6 and 10.
4. A method according to any one of the preceding claims, characterized in that as solvent an organic solvent is used or a two-phase solvent with a phase transfer agent is used.
- 15 5. A method according to any one of the preceding claims, characterized in that an aprotic polar solvent is used.
6. A method according to claim 5, characterized in that DMF is used as solvent.
7. A method according to claim 4, characterized in that a  
20 quaternary ammonium salt is used as phase transfer agent.
8. A method according to any one of the preceding claims, characterized in that alkenes are used as non-activated compounds containing unsaturated carbon bonds.
9. A method according to any one of claims 1-7,  
25 characterized in that alkadienes are used as non-activated compounds containing unsaturated carbon bonds.
10. A method of preparing polymeric polysulfides, characterized in that non-activated alkadienes react with monohydrogen polysulfide.
- 30 11. A method of preparing heterocyclic sulfur compounds, characterized in that alkadienes with a chain of at most 3 carbon atoms between carbon atoms which are attached to

another carbon atom through an unsaturated bond react with monohydrogen polysulfide.

12. A method of vulcanizing rubber, characterized in that rubber reacts with monohydrogen polysulfide.

## INTERNATIONAL SEARCH REPORT

Internationa l Application No PCT/NL 93/00254
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A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 C07B45/06 C07C319/22 C08G75/14 C07D335/02 C07D339/00  
 C07D339/04 C07D337/04 C08J3/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 5 C07B C07C C08G C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>ORGANIC GEOCHEMISTRY            vol. 11, no. 6 , 1987 Oxford, GB,            pages 563 - 571            R.L. LALONDE, ET AL.: 'Low-temperature,            polysulphide reactions of conjugated ene            carbonyls: a reaction model for the            geological origin of S-heterocycles'            cited in the application            see page 566, right column            ---            -/--</p>	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

8 March 1994

Date of mailing of the international search report

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 60, no. 10 , October 1938 Washington, DC, US, pages 2452 - 2455 S.O. JONES, ET AL.: 'The addition of sulphur, hydrogen sulphide and mercaptans to unsaturated hydrocarbons' see page 2454, right column - page 2455, left column ---	1
A	WO,A,92 03524 (MOBIL OIL) 5 March 1992 see examples 1-3 ---	1,2
A	GB,A,450 760 (I.G. FARBENINDUSTRIE) 20 August 1936 see the whole document ---	1
A	US,A,3 333 008 (A. LANG et al.) 25 July 1967 see the whole document ---	1
P,X	GEOCHIMICA ET COSMOCHIMICA ACTA, vol. 56, no. 12 , December 1992 Oxford, GB, pages 4321 - 4328 W. DE GRAAF, ET AL.: 'Laboratory simulation of natural sulphurisation: I. Formation of monomeric and oligomeric isoprenoid polysulphides by low- temperature reactions of inorganic polysulphides with phytol and phytadienes' see the whole document -----	1,2,5,6, 8,9,11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 93/00254

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9203524	05-03-92	EP-A- 0544745	09-06-93
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GB-A-450760		NONE	
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US-A-3333008		BE-A- 650101	
		DE-B- 1234210	
		FR-A- 1393251	
		GB-A- 1067378	
		LU-A- 46442	01-01-72
		NL-A- 6407564	06-01-65
		OA-A- 266	15-05-66
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