

Bis(2,3-dimethylbutenyl)sulfanes, the Products of Sulfane Addition to 2,3-Dimethyl-1,3-butadiene and of the Reaction of Sulfur with 2,3-Dimethyl-2-butene.

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Abstract: The reaction of sulfanes (H_2S_n , $n > 1$) with 2,3-dimethyl-1,3-butadiene (DMBD) yields 3 sets of products; bis(2,3-dimethyl-2-buten-1-yl)sulfanes **1** as the main product, and two minor products (2,3-dimethyl-2-buten-1-yl)(2,3-dimethyl-1-buten-4-yl)sulfanes **2** and (2,3-dimethyl-2-buten-1-yl)(2,3-dimethyl-1-buten-3-yl)sulfanes **3**. The reaction of sulfur with 2,3-dimethyl-2-butene (a low molecular weight model for unsaturated rubber), in the presence of zinc oxide and an accelerator yields also **1** as the major product and **3** as a minor product, but not product **2**. The mechanisms of both reactions, i. e. **addition** in the first case and **substitution** in the second case, are discussed.

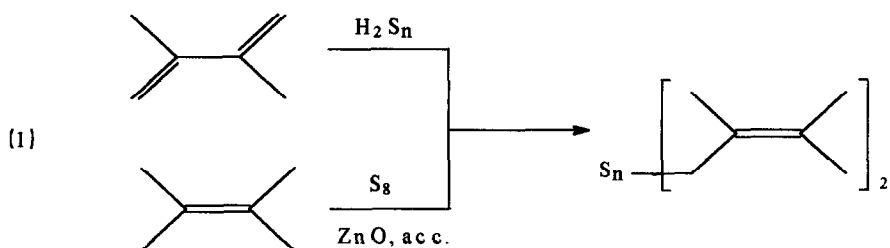
Introduction

The addition reaction of sulfanes H_2S_n with conjugated dienes provides a new method of forming CS_n bonds of well-defined chain length n in an one step reaction.¹ In the case of 2,3-dimethyl-1,3-butadiene (DMBD) as diene component the addition reaction was studied in more detail. Typically it proceeds under complete retention of the sulfur chain length n , which is determined by the starting sulfane molecule. Furthermore, 1,4-addition predominates, leading in first approximation to the formation of one isomer. For this reason, in addition to its preparative versatility, this addition reaction can be used to analyze the chain length distribution of sulfane mixtures: The sulfane mixture is first transformed into the corresponding bis(2,3-dimethyl-2-buten-1-yl)sulfane mixture, which is then analyzed by reversed phase HPLC.² Bis-2-alkenylsulfanes represent model compounds for rubber vulcanizates, which contain analogous sulfur bridges in allylic position to the double bond in the polymer chain. Thus the addition reaction constitutes a new preparative approach to these model compounds.

Vulcanization with sulfur systems is still the most important method to crosslink unsaturated

rubbers.³ The chemistry of the crosslink reaction and the structure of the sulfur crosslinks have been studied extensively, especially for natural rubber,⁴ although many details are still unknown. For this rubber type, model vulcanization studies with 2-methyl-2-pentene were carried out and provided detailed knowledge of the crosslink structure.⁵ As well as giving structural information, model vulcanizates may also provide statements on the influence of changes in vulcanization conditions, as reported by Lautenschlaeger.⁶

The sulfur vulcanization of 2,3-dimethyl-2-butene in the presence of zinc oxide and an organic accelerator yields bis(2,3-dimethyl-2-buten-1-yl)sulfanes as its main product, as expected.⁷ Thus, the substitution reaction of the sulfur vulcanization gives the same main products as were obtained by the sulfane addition to 2,3-dimethyl-1,3-butadiene (see equation 1).



In both reaction mixtures minor isomeric products are found. In spite of the fact that these reactions are executed at completely different conditions the isomers seemed to be similar. In addition to the characterization of the main products it is the aim of the present study to find out the nature and conditions of formation of the minor products of both reaction types and to determine the mechanism of the isomerization reaction.

Results and Discussion

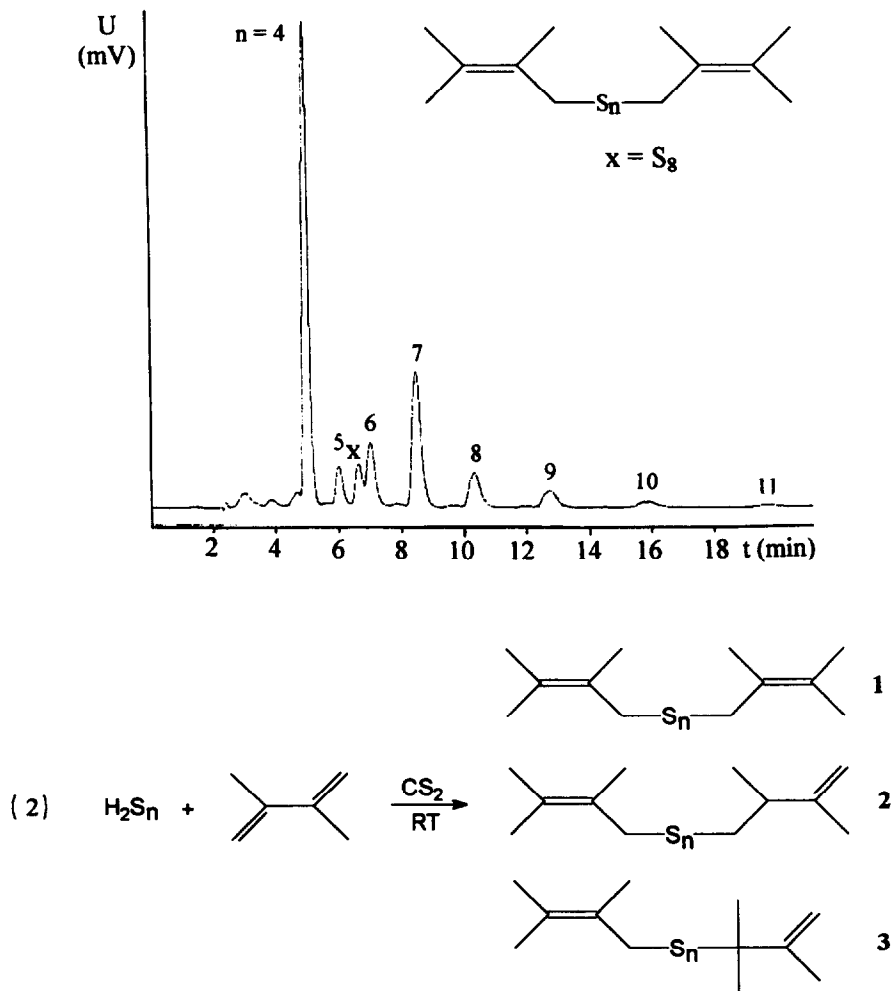
a) Generation of Diorganylsulfanes by Sulfane Addition

The reaction of crude H_2S_4 , obtained from the condensation reaction of a large surplus of H_2S with S_2Cl_2 ,⁸ with DMBD in CS_2 yields a yellow oil after removing the solvent from the reaction mixture. Characterization of this oil by RP-HPLC shows that beside the expected dialkenyltetrasulfane also molecules with a larger sulfur chain are formed (Figure 1). The assignment of the peaks is in accordance with a linear correlation between the chainlength (S_n) and $\log k'$ found by Möckel.⁹ Furthermore, the enhanced intensity of the R_2S_7 -peak agrees well with the fact that heptasulfane can be formed by the reaction of two molecules of S_2Cl_2 with three molecules of dihydrogen sulfide and not only by disproportionation. Disproportionation, which does not occur during the addition reaction, cannot be avoided during the condensation reaction of dihydrogen sulfide with dichlorosulfanes.⁸

The structural identification of the alkenyl sulfanes responsible for the main peaks of the chromatogram as bis(2,3-dimethyl-2-buten-1-yl)sulfanes 1 (see equation 2) was carried out by the separation of several selected sample fractions through preparative HPLC, followed by ^1H and ^{13}C NMR as well as mass spectroscopy. In the HPLC chromatogram so-called satellite peaks, at least one before every main peak, are visible (relative intensity $\approx 3\%$). Using the same method as above the satellite peaks

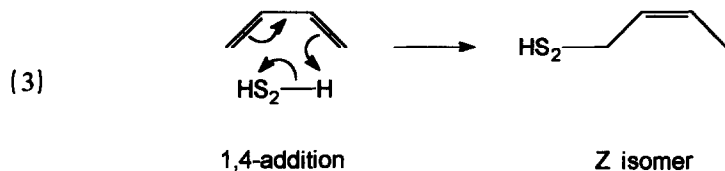
could be shown to originate from the isomers 2 and 3 (see equation 2), which are present with the relative abundances of 0.02 : 0.01 (relative abundance of isomer 1 = 1).

Figure 1: HPLC chromatogram of the reaction mixture of H_2S_n and 2,3-dimethyl-1,3-butadiene



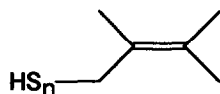
In comparison with dihydrogen sulfide and thioles the polysulfanes are more reactive towards diene systems. This increase in reactivity must be related to the higher acidity of sulfanes ($K_a(H_2S) = 9.1 \times 10^{-8}$; $K_a(H_2S_3) = 6.3 \times 10^{-5}$).¹⁰ The higher proton activity implies a high concentration of HS_n^- which represents a strong nucleophile. In general, sulfane addition to conjugated dienes may occur through an ionic, a synchronous, or a radical mechanism. Since the addition reaction is carried out in the dark at room temperature the formation of radicals is unlikely. A synchronous mechanism can be excluded at least for the 1,4-addition referring to the products from the reaction of disulfane with 1,3-butadiene.¹ The main

product obtained is bis(2-buten-1-yl)disulfane showing E configuration in contrast to Z configuration, which must be expected for a synchronous mechanism.

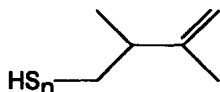


Considering the fact that the acidity of sulfanes is comparable to that of acetic acid an ionic mechanism appears most favourable. After the dissociation step the resulting HSn^- -ion may attack as nucleophile, but on the other hand the reaction may also start with an electrophilic attack of the acidic proton. In order to distinguish between these two possibilities the regioselectivity of the addition reaction must be considered. In a polar reaction the following pathways may occur:

- (i) 1,4-addition of H_2S_n to DMBD yields (2,3-dimethyl-2-buten-1-yl)sulfanes,



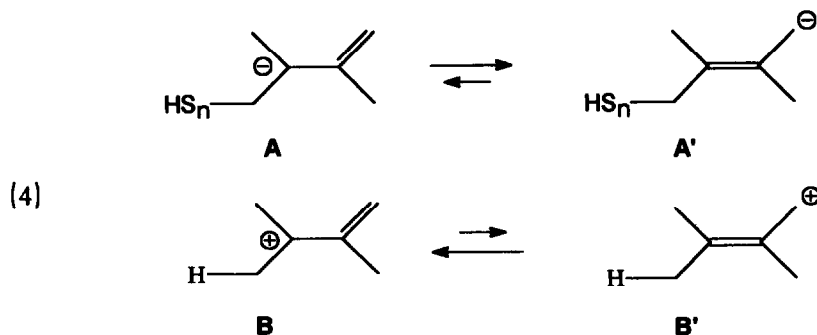
- (ii) 1,2-addition in the anti-Markovnikov sense leads to the formation of (2,3-dimethyl-1-buten-4-yl)sulfanes,



- (iii) 1,2-addition according to Markovnikov's rule gives (2,3-dimethyl-1-buten-3-yl)sulfanes.



Since the products of 1,4-addition to DMBD are the same for an electrophilic and a nucleophilic reaction, only the investigation of the isomeric distribution of the small amount of products resulting from 1,2-addition helps to clarify the mechanism. Taking into account the predominant influence of allylic stabilization, two intermediates resulting either from nucleophilic or from electrophilic attack are of special interest.



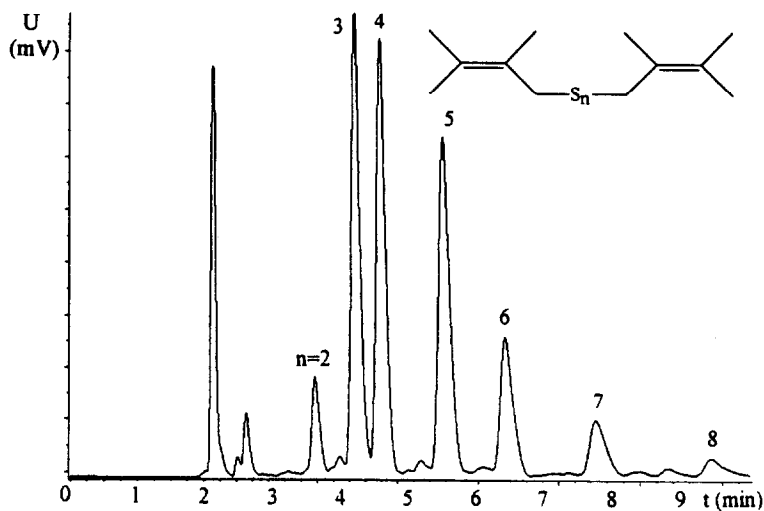
As can easily be seen only nucleophilic 1,2-addition (intermediate A) leads to the anti-Markovnikov product, which is found to be the major component of the isomers formed by 1,2-addition. The assumption of a nucleophilic addition mechanism is also in agreement with the observed preference of 1,4-addition. The corresponding product may result from the intermediates A' and B' of which A' is the more stable form in the mesomeric equilibrium.

b) Generation of Diorganylsulfanes by Vulcanization

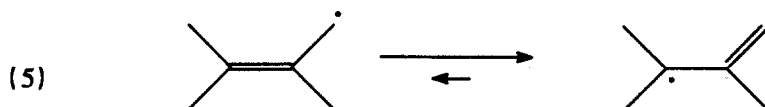
After heating a mixture of 2,3-dimethyl-2-butene (tetramethylethylene = TME), zinc oxide, sulfur and the accelerator tetramethylthiuram disulfide, $[\text{Me}_2\text{NC}(\text{S})\text{S}]_2$ (TMTD), for 1 h at 140°C , a suspension of a white solid in a yellow liquid is obtained.⁷ The mixture is separated by filtration. The infra-red spectrum of the white solid indicates the presence of zinc oxide, zinc sulfide and zinc dimethyldithiocarbamate, $[\text{Me}_2\text{NC}(\text{S})\text{S}]_2\text{Zn}$. The latter is known to be formed from zinc oxide and TMTD.^{11,12} Column chromatography of the liquid phase of the product mixture with n-pentane as the mobil phase and silicagel as the stationary phase yields a slightly yellow oil. RP-HPLC analysis of this oil gives a chromatogram (Figure 2) similar to that obtained for the addition reaction of the sulfanes. Even the satellite peaks are present with nearly the same intensity ($\approx 3\%$). Using the same analytical method as for the products of the sulfane addition it could be shown, that the main and satellite peaks are caused by the isomers 1 and 3, respectively.

Vulcanization of model olefines used in earlier experiments gave a large variety of products,¹² resulting from the availability of geometrically different but nearly equally reactive sites for proton-sulfur-substitution. Moreover, a shift of the double bond during the substitution reaction or thereafter had no significant influence on the free energy of formation of the resulting product. In contrast, the four methyl groups of TME, the model olefin selected by us, are geometrically equivalent when reacting with sulfur. Therefore the only possibility leading to isomerization is a shift of the double bond, although this is quite unfavourable for energetic reasons. From the latter it may be concluded that the formation of 3 results from a kinetically controlled reaction rather than from a thermodynamically controlled one. This is in agreement with the fact that pure 1 ($n=3$), which was obtained from a semi preparative HPLC separation, did not show any isomerization after heating to 140°C for 1h.

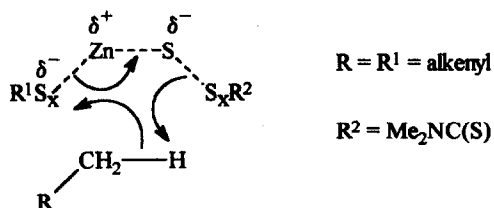
Figure 2: HPLC chromatogram of the purified reaction mixture of S₈, TMTD, ZnO and 2,3-dimethyl-2-butene



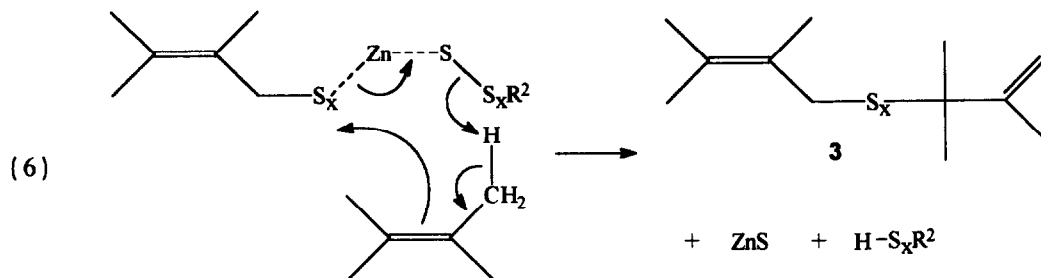
Since the product distribution of a radical vulcanization mechanism would depend on the following equilibrium



a thermodynamic control should be expected in this case. As this was not observed a radical mechanism can be excluded. This agrees well with the result of a more detailed discussion of Bateman¹³ on the basis of earlier results from model vulcanization where the polar mechanism was assumed to proceed via an electrocyclic transition state similar to that shown below.



If the double bond is allowed to take part in this transition state, this will immediately lead to the formation of 3.



A second possibility of a kinetically controlled formation of 3, involving a quite similar transition state, is the accelerator-assisted sulfur degradation of long-chain sulfur bridges¹² formed in the early stage of the vulcanization process. Although this degradation process should cause an increase of the isomeric ratio 3(i)/1(i) with decreasing length $n=i$ of the sulfur chain, the opposite result is found experimentally: For our standard vulcanization conditions (see experimental section below) the molar ratio 3(i)/1(i) was found to increase from about 0,013 to 0,035 with the chain length n increasing from 2 to 5. Although we have not yet found an explanation for this effect, it seems to contradict the assumption that the accelerator-assisted sulfur degradation is the major source of a shift of the double bond during vulcanization. Therefore, we assume that isomer 3 is predominantly produced according to equation (6).

Conclusions

Reaction between H_2S_n and DMBD yields 1 as the main product. This product is formed as the result of a double 1,4-addition of H_2S_n with two molecules of the diene. The isomeric product 2 stems from an 1,2-addition, in the anti-Markovnikov sense, of H_2S_n towards one molecule of the diene. Also a third isomer 3 is found, which is formed in the course of an 1,2-addition of H_2S_n towards one of the diene molecules according to the Markovnikov rule. Since the anti-Markovnikov products show the higher molar ratio, it can be concluded that the nucleophilic attack must predominate. Sulfur vulcanization of TME leads only to two types of isomers: 1 as main product and 3 as byproduct. The presence of 3 in the vulcanization products must be ascribed to a 1,3-shift of the double bond during the proton-sulfur substitution.

EXPERIMENTAL

Starting Materials and Spectral Equipment:

DMBD was distilled through a Vigreux column before it was used in addition reactions.

Commercial TME (Aldrich, 98% purity) contained several isomers as impurities, which would lead to many unwanted vulcanization products. Purification to a sufficient grade was achieved by distillation through a Spaltrohr column.

The distilled substances were checked by proton NMR and RP-HPLC before they were used in reactions. All solvents were dried and distilled before use, HPLC solvents were purified by distillation.

Nuclear Magnetic Resonance:

Proton NMR spectra were recorded at 200 MHz on a Bruker AC 200 FT spectrometer or a Joel FX-200 FT spectrometer and at 300 MHz on a Bruker WM 300 or an AMX 300 FT spectrometer, using 5 mm sample tubes and CDCl_3 , CHCl_3 as internal reference.

The ^{13}C NMR spectra were recorded at 75 MHz on a Bruker AMX 300 FT spectrometer.

High Performance Liquid Chromatography:

The HPLC equipment used at the Universität zu Köln consisted of a Bruker LC 21C quarternary gradient solvent system, a LC 313 variable wavelength UV/VIS detector and a LC 42 ChromStar chromatography and data system. The HPLC equipment used at Leiden University consisted of a Gilson 302 Piston Pump with Manometric Module 802C, a Linear UVIS 203 absorbance detector and the JCL6000 chromatography data system, produced by Jones Chromatography, in combination with a Rheodyne injection valve (type 7125). For chromatographic conditions see table 1.

Addition Reaction of Crude H_2S_4 to 2,3-Dimethyl-1,3-butadiene:

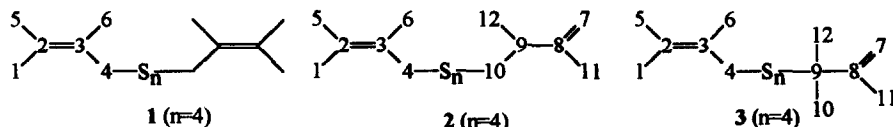
The H_2S_4 sample was synthesized from the condensation reaction of 114 g (3.35 mole) H_2S (liq.) with 10 g (0.074 mole) S_2Cl_2 . The ratio of the main products H_2S_4 and H_2S_7 was found to be 2.3 : 1 by ^1H NMR spectrum (H_2S_7 is formed in the side reaction between the intermediate HSSSCl and H_2S_4 ; to avoid this reaction an even larger excess of H_2S is necessary). The bis(2,3-dimethyl-2-buten-1-yl)sulfanes are typically synthesized by reacting 40 mmol H_2S_n (in the case of mixtures the medium chain length n is estimated from the proton NMR spectra) with 88 mmol (10% excess) of DMBD. The diene is added slowly (within 10 min) to the sulfane solution in 8 ml carbon disulfide. During the addition the reaction mixture is cooled with an ice bath. After two h of stirring at room temperature the solvent and the excess of the diene are distilled off. The product is a pale yellow oil, which gives rise to the HPLC chromatogram shown in Figure 1. Two fractions were separated by preparative RP-HPLC containing the main product (1, $n = 4$) and its isomers (2 and 3, $n = 4$), respectively. The structural characterization of pure 1 and the mixture of 2 and 3 was carried out by ^1H and ^{13}C NMR spectroscopy.

Sulfur Vulcanization of Tetramethylethylene:

0.15 g (0.59 mmol) sulfur, 0.15 g (0.69 mmol) TMTD and 0.5 g (6.14 mmol) zinc oxide were added to 2 ml (16.86 mmol) of TME. The vulcanization was carried out in a vessel with a screw cap, closed by a Teflon Mininert valve. The reaction was started by placing the vessel in an oil bath kept at 140°C ; during the reaction the mixture was stirred. The reaction was stopped after 1 h by removing the vessel from the oil bath and allowing it to cool down to room temperature. After filtration a clear yellow liquid was obtained, leaving a colourless solid. The reaction mixture was separated by column chromatography using Silicagel 60 as the stationary phase. With *n*-pentane as the mobile phase a yellow fraction was obtained. Evaporation of the eluent gave a yellow oil which consisted of 1 and 3.

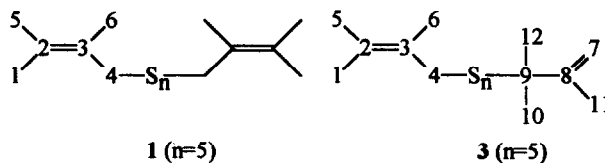
Table 1: Conditions for the HPLC chromatograms.

	Figure 1	Figure 2	preparative separation
Column	Spherisorb ODS II 5 μm , 250 x 4 mm	Spherisorb ODS II 5 μm , 250 x 4 mm	Spherisorb ODS II 5 μm , 250 x 20 mm
Solvent	t-butylmethyl ether/ methanol	t-butylmethyl ether/ methanol	10 % t-butylmethyl ether
Eluent	100% methanol isocratic	100% methanol isocratic	95% methanol, 5% H ₂ O isocratic
Injection volume	20 μl	20 μl	70 μl
Flow rate	1 ml/min	1 ml/min	10 ml/min
Detector wavelength	254 nm	254 nm	254 nm

Table 2: ¹H- and ¹³C NMR shifts (ppm) of the tetrasulfanes (in CDCl₃) of the different isomers obtained from the addition reaction of H₂S_n to DMBD.

Number of atom	1:		2:		3:	
	¹ H NMR	¹³ C NMR	¹ H NMR	¹³ C NMR	¹ H NMR	¹³ C NMR
1	1.75	21.2	1.75	21.2	1.75	21.2
2	-	132.0	-	131.9	-	131.3
3	-	122.2	-	122.3	-	122.4
4	3.69	44.1	3.69	44.1	3.69	43.4
5	1.75	20.9	1.75	20.9	1.75	21.1
6	1.69	18.2	1.69	18.3	1.69	18.3
7	-	-	4.77	111.2	4.95	114.0
8	-	-	-	147.6	-	147.2
9	-	-	2.55-2.66	40.5	-	56.0
10	-	-	2.84-3.15	45.1	1.48	27.2
11	-	-	1.70	19.7	1.83	20.0
12	-	-	1.11/1.15	18.8	1.48	27.2

Table 3: ^1H NMR shifts (ppm) of the pentasulfanes (in CDCl_3) of the different isomers obtained from the reaction of S_g and 2,3-dimethyl-2-butene in the presence of TMTD and ZnO.



Number of atom	1	3
1	1.76	1.76
4	3.71	3.71
5	1.76	1.76
6	1.69	1.69
7	-	4.99
10	-	1.48
11	-	1.84
12	-	1.48

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