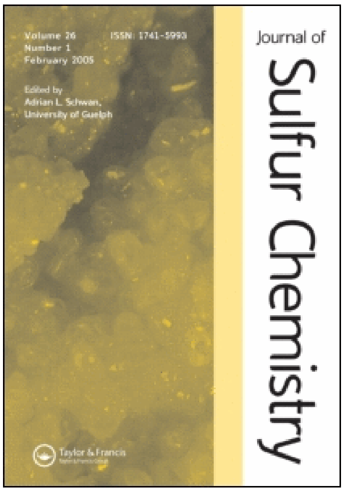

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Probing the chemistry of rare sulfur allotropes: S_9, S_{12} and S_{20}

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Probing the chemistry of rare sulfur allotropes: S_9, S_{12} and S_{20}

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Sulfur allotropes S_9, S_{12} and S_{20} were prepared to examine their sulfur-transfer properties in reactions with various alkenes and dienes. All three molecules underwent decomposition and were successfully trapped. The S_{12} and S_{20} molecules delivered similar products in respectable yields. With dienes, an S_2 fragment was preferentially secured with the cyclic tetrasulfide being a minor product. S_{20} was trapped by norbornene to give the tri- and pentasulfides in good yield. In the case of S_9, yields of the trapped products were not as high as with the larger allotropes, although S_9 with norbornene delivered the corresponding episulfide. Overall, these three allotropes are not as effective as S_{10} as sulfurating agents.

Keywords: sulfur allotrope; sulfuration; S_9; S_{12}; S_{20}

1. Introduction

The first-ever synthesis of *cyclo*-nonasulfur, S_9, was performed by Schmidt using titanocene pentasulfide (**1**) (*1*), which was reacted with dichlorotetrasulfane, S_4Cl_2, under analogous conditions developed by Schmidt *et al.* (*2*) for accessing other sulfur homocycles. It was only 15 years later that Steudel *et al.* (*3*) discovered that S_9 can actually crystallize in two polymorphic states, α- and β-S_9. Slight modifications to the initial synthetic method allowed for the isolation of pure α-S_9 (*3*). Steudel *et al.* also found that β-S_9 could be isolated as a remnant byproduct upon S_9 treatment with trifluoroperacetic acid, which affords S_9O. The elucidation of each of the two polymorphs of S_9 was deduced by the Raman spectroscopy. The structure of α-S_9 was later confirmed by single crystal X-ray diffraction (*4*). α-S_9 belongs to the less symmetrical group of sulfur homocycles, with alternating bond lengths and great variations in torsion angles. To our knowledge, no single crystal structure for β-S_9 has been obtained to date.

Cyclo-nonasulfur has also been quantified as a component of liquid sulfur (*5*) and has been detected as a minor impurity in solid commercial samples of S_8 (*6*). Photochemical decomposition of S_7 and S_8 in CS_2 (*7*), thermal decomposition of S_8 in CS_2 (*8*) and thermal thermal depolymerization of industrial polymeric sulfur S_μ (*9*) have all resulted in the detection of S_9. *Cyclo*-nonasulfur is also a component of the mixtures of sulfur allotropes produced by the acid

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decomposition of thiosulfate (*10*) or by the reaction of SCl_2 with aqueous KI (*11*). The last two reactions produce S_6 as their main component. S_9 has also been detected by high pressure liquid chromatography (HPLC) analysis in the thermal decomposition of trityldithiosulfenyl chloride (*12*). Finally, S_9 has also been detected in a reaction involving titanocene dicarbonyl, S_6 and SCl_2 (*13*). The only account where S_9 is used as a reagent appears to be the formation and characterization of *cyclo*-nonasulfur oxide, S_9O (*3*).

Both S_{12} and S_{20} have also have also been successfully extracted from sulfur melts (*14*, *15*), though the first-ever account of a sulfur allotrope extraction from liquid sulfur was actually reported by Schmidt and Block (*16*) years earlier for S_{12}; this initial paper remains very controversial as the method was never repeated successfully. S_{12} and S_{20} have both been initially prepared by the methatetic method of Schmidt and Wilhelm (*17*). The most efficient procedure for S_{12} and S_{20} synthesis involves the use of **1** as a 5-sulfur source. Both S_{12} (*2*) and S_{20} (*18*) are isolated as side products in the reactions leading to the synthesis of S_6 and S_{10}, respectively; isolated yields for S_{12} and S_{20} using this method are 11% and 8%, respectively. S_{12} and S_{20} have also been produced in low yields (1–2% for S_{12} and 0.4% for S_{20}) by the reaction of S_2Cl_2 with aqueous KI (*19*), which mainly affords S_6. Finally, slow decomposition of S_8O at −20°C in CS_2 produces small amounts of S_{12} (*20*). The structures of both S_{12} and S_{20} have been determined by single crystal X-ray diffraction. S_{12} belongs to the group of highly symmetrical sulfur rings with similar structural parameters to S_8. This and its high melting point (M_P) (vide supra) distinguishes S_{12} as the second most stable allotrope after S_8. S_{20}, on the other hand, belongs to the less symmetrical group of sulfur rings that possesses alternating bond distances and large variations in their torsion angles, similar to those parameters observed for S_9. To our knowledge, neither S_{12} nor S_{20} has been investigated for their sulfur-transfer capabilities.

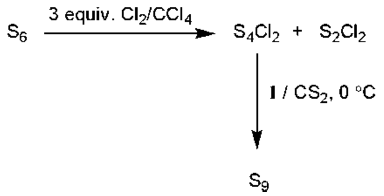
Herein, we report our initial investigation into the sulfuration ability of each of S_9, S_{12} and S_{20} with 1,3-dienes and strained olefins and contrast these with more commonly used S_8 and S_{10}.

1.1. *Synthesis and characterization of sulfur allotropes*

The synthetic route that was chosen in this study in order to produce *cyclo*-S_9 combined two procedures. Dichlorotetrasulfane (S_4Cl_2) was synthesized according to Steudel *et al.*'s procedure (*21*) and not the older procedure of Fehér *et al.* (*22*). Steudel found that the chlorination of *cyclo*-hexasulfur, S_6, with excess chlorine (3 equiv. Cl_2) generates a mixture of S_4Cl_2 and S_2Cl_2. The latter can be distilled off under reduced pressure, and a relatively pure sample of S_4Cl_2 is thus obtained as a malodorous orange oil in a reported 62% yield. Chlorine was dispensed in solution in carbon tetrachloride (CCl_4). These Cl_2/CCl_4 solutions were prepared by bubbling chlorine gas into the solvent and were always used immediately after their preparation; the loss of Cl_2 gas from the CCl_4 solution was observed over time. In the course of this study, S_4Cl_2 was obtained in average yields of 47%, in relatively good agreement with Steudel.

Dichlorotetrasulfane obtained by this method was of sufficient purity to be directly reacted with titanocene pentasulfide (**1**) (*23*), and α-S_9 was obtained as a bright yellow solid that was then recrystallized from CS_2/n-pentane (Scheme 1). Pure α-S_9 was thus obtained in 21% yield (MP 61–63°C), comparable to the yields of 30% (*1, 3*) and 18% (*21*) that had previously been reported. Solid α-S_9 was found to decompose rapidly at room temperature or with light. Samples were thus kept in the dark at −40°C, and even freshly recrystallized samples were often not fully soluble in CS_2. A small fraction of insoluble polymeric sulfur always seemed to be present.

The characterization of α-S_9 was achieved by the FT-Raman spectroscopy and the purity of the samples was also assessed by HPLC. The main vibrational bands for α-S_9 synthesized in the course of this study align with those reported previously and the identity of the sample can be ascertained to a high degree of certainty by the strongly overlapping Raman spectra (Table 1) (*24*).



Scheme 1. Preparation of α-S_9 from S_6.

1

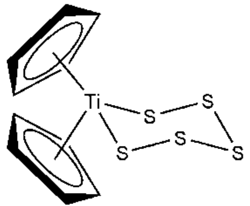


Table 1. Raman spectra of α-S_9.

α-S_9^a			α-S_9^b		
	298.5(10)	Shoulder	485(10)	297(13)	117(31)
477(23)	257(13)		477(16)	256(12)	111(sh)
	245(26)	105.5(67)	463(sh)	245(23)	104(58)
456(100)			454(100)	222(26)	100(sh)
	219(38)	80(62)	442(sh)	215(31)	78(67)
437(44)	186(72)		436(49)	188(90)	57(50)
417(10)			416(11)	181(sh)	46(33)
	160.5(46)			161(37)	43(sh)
	157(38)			155(28)	41(sh)
				151(sh)	27(35)

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature; [b] Ref. (*3*); Cary 82 Raman spectrometer/Krypton laser/647 nm/1.5 cm^{-1}/−100°C.

The purity of each S_9 sample was corroborated by reverse phase HPLC (Figure 1). Apart from the insoluble polymeric sulfur fraction mentioned above, no sulfur cycle other than *cyclo*-S_9 could be detected in each of the different batches used.

Two synthetic methods were used in the course of this study for the formation of S_{12}, whereas only one method was used for the generation of S_{20}. S_{12} was first synthesized by extraction from liquid sulfur in only 0.08% yield, comparable but less than what was reported by Steudel and Mäusle (0.2%) (*14, 15*). In contrast to the complicated custom-made apparatus (*15*) designed by Steudel, the experimental setup used in this study was much simpler: elemental sulfur (S_8) was heated by oil bath in a beaker and the contents of the beaker simply poured into liquid nitrogen when appropriate. The relative drop in the observed yield is most likely accounted for by the fact that the temperature stabilization of the melt was not accurately maintained and the rate of liquid nitrogen-promoted quenching was not as efficient as in the work of Steudel.

In order to obtain greater quantities of S_{12}, we turned to the work of Schmidt *et al.* (*2*), wherein, S_{12} is a side product of the reaction between **1** and sulfur dichloride (SCl_2) that mainly produces S_6. Notwithstanding, yields for S_{12} obtained by this method averaged 8%, in agreement with the 11% yield reported by Schmidt.

S_{20} was prepared through the reaction between **1** and sulfuryl chloride (SO_2Cl_2). The experimental procedure that allows for the direct isolation of pure S_{20} in 8% yield was not used (*18*). S_{20} was instead collected over time, as the side product obtained from the procedure designed to prepare S_{10} (*2, 25*). S_{20} was separated from S_{10} by exploiting its solubility difference in CS_2. Yields for S_{20} using this extraction technique averaged 5%. S_{20} batches were then purified either by recrystallization from CS_2 or simply washed at room temperature with CS_2 in order to remove any remaining S_{10}. Recrystallization was avoided mostly as large amounts of very flammable CS_2 were required to fully solubilize S_{20}.

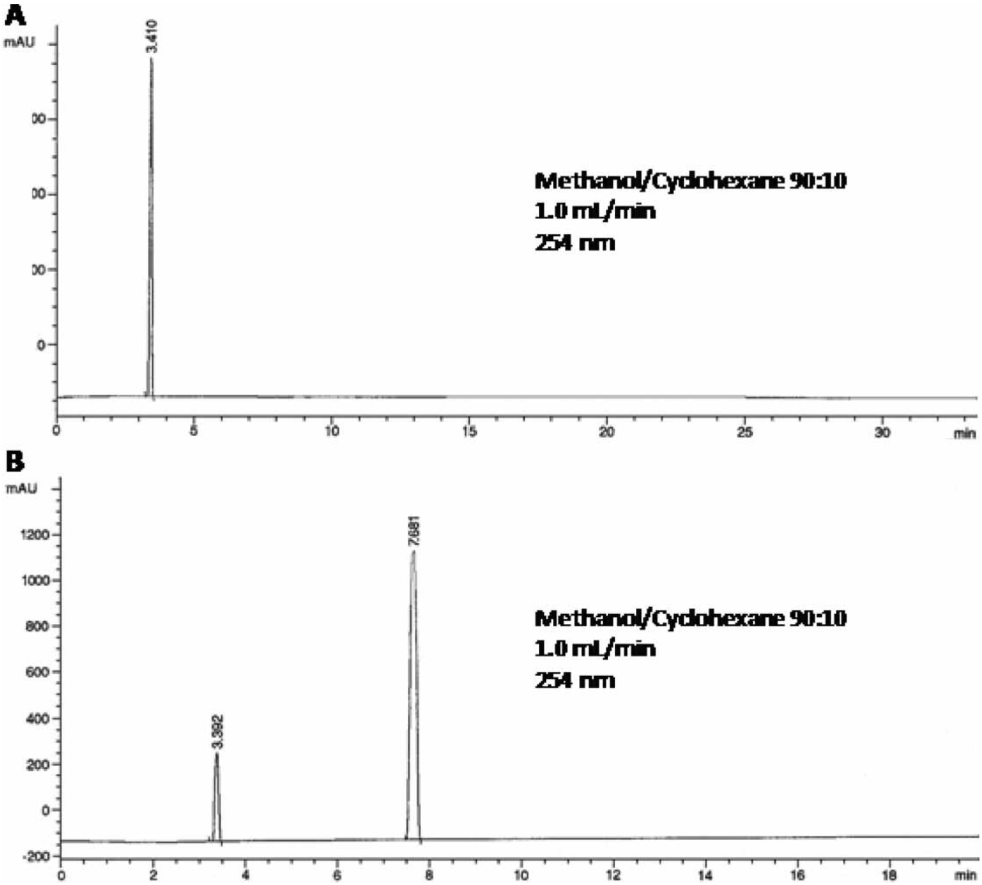


Figure 1. Reverse phase HPLC traces of (A) control CS_2 and (B) CS_2 and α-S_9.

Table 2. Raman spectra for S_{12}.

S_{12}^{a}			S_{12}^{b}		
	289(13)	127(80)	475(vw)	289(m)	127(vs)
459(100)	243(17)		460(vs)	245(m)	67(s)
448(35)	Shoulder	64(32)	449(s)	238(m)	63(vs)
				221(vvw)	58(m–s)
				180(sh)	43(vs)
				177(m–s)	31(vs)
	177(22)			170(m)	
	Shoulder			156(vvw)	

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature; [b] Ref. (*24*); Cary 82 Raman spectrometer/Krypton laser/647 nm/1.5 cm^{-1}/ − 80°C.

As with α-S_9, the identification and characterization of S_{12} and S_{20} were achieved by the FT-Raman spectroscopy. Tables 2 and 3 report the positions of the main vibrational modes observed for S_{12} and S_{20}, respectively, and their respective spectra were compared with those previously reported (*20, 24, 26*). Representative HPLC runs for S_{12} and S_{20} are reported in Figure 2 and attest to the purity of each sample; small amounts of residual S_8 could occasionally be detected along with the desired sulfur allotrope.

Table 3. Raman spectra for S_{20}.

S_{20}^{a}			S_{20}^{b}		
	270(28)		470.5(41)	270(26)	113(4)
466.5(100)		95(59)	466(100)	254(sh)	93(63)
	251(28)	67(31)	462(sh)	250(24)	66(46)
			454(9)	213(5)	54(31)
			444(17)	207(5)	48(17)
444(20)	208(8)		428(8)	188(12)	40(sh)
427(10)	187(15)		416(3)	173(5)	32(34)
			411(3)	167(16)	29(sh)
	169(20)			136(73)	18(7)
	137(64)				

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature. [b] Ref. (*15*); Cary 82 Raman spectrometer/Krypton laser/647 nm/1.5 cm^{-1}/−100°C.

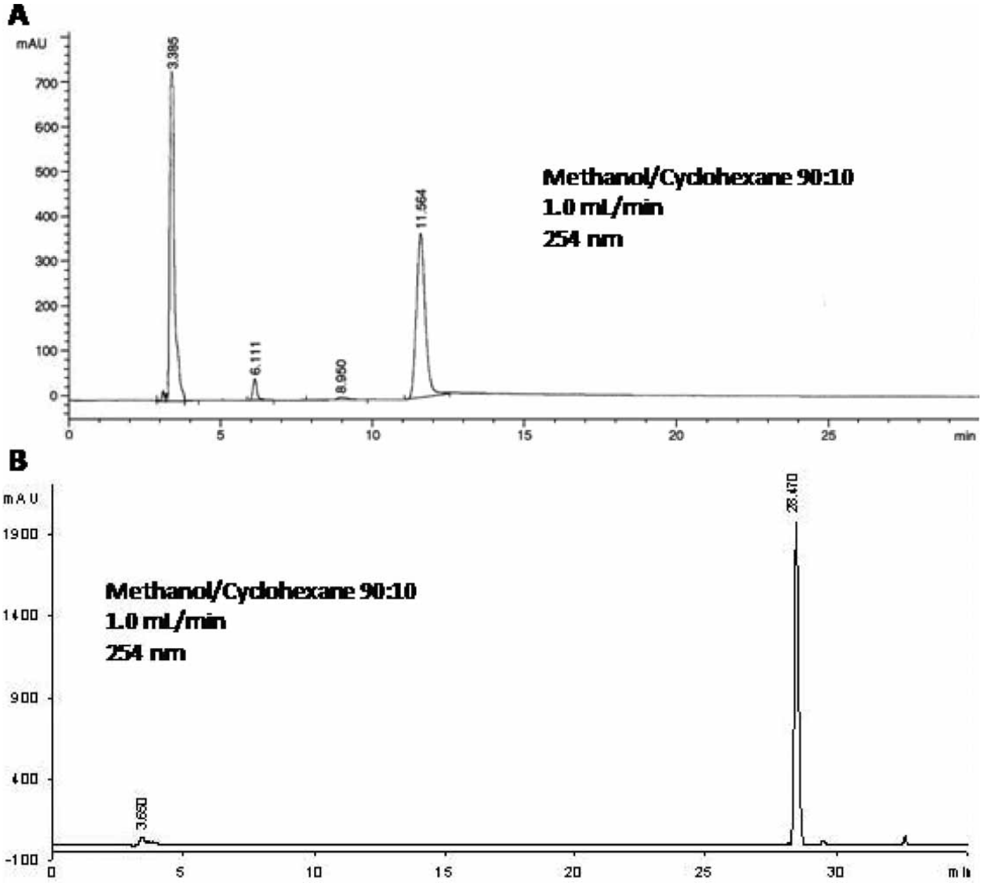
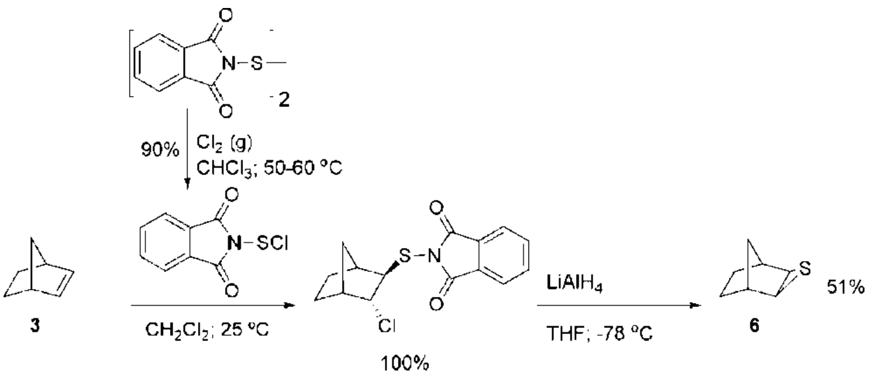


Figure 2. Reverse phase HPLC traces of (A) S_{12} and (B) S_{20}. CS_2 serves as an internal standard.

1.2. *Independent synthesis*

In order to assess sulfur allotrope reactivity properly with 2,3-diphenylbutadiene (**2a**), 2,3-dimethylbutadiene (**2b**) or norbornene (**3**), independent syntheses of products **4-8** were required. The preparation of all the products except **6** has previously been reported (*27*). The synthesis of *exo*-2,3-epithionorbornane (**6**) was accomplished using phthalimido-*N*-sulfenyl chloride as the sulfur-transfer reagent, itself derived from *N*, *N*′-dithio-*bis*(phthalimide) (*28*) (Scheme 2) (*29*).



Scheme 2. Parallel synthesis of *exo*-2,3-Epithionorbornane **6**.

1.3. *Reaction of* S_9 *with (2a and 2b) and norbornene (3)*

In this study, *cyclo*-nonasulfur S_9 was reacted with three key substrates (two dienes and a strained olefin) in order to probe its reactivity as a sulfurating agent. Due to the difficulty in preparing S_9, these reactions were carried out on a small scale. Yields were measured by comparison with an internal standard, and the identity of the different products was determined by spectroscopic comparison with authentic samples, which were synthesized separately. These trapping reactions constitute a good starting point in order to compare the difference in reactivity and/or product formation propensity between the different sulfur allotropes.

The experimental protocol used in the reactions between S_9 and these substrates involved the reaction of equimolar amounts of 1,3-dienes **2a** or **2b** or norbornene (**3**) with S_9 at high temperatures in non-polar media. The sulfur allotrope was predissolved into an appropriate amount of carbon disulfide (CS_2) and added to the refluxing olefin. Reactions were terminated when S_9 was no longer detected by reverse phase HPLC and reaction times never exceeded 3 h. Product distribution and yields were determined by ^1H NMR spectroscopy in the presence of 9-methylanthracene as the internal standard.

The results obtained from these trapping studies are reported in Table 4 and Table 5 reports two control reactions that were carried out with S_8 as the sulfurating agent; in order to properly compare 'S' stoichiometry, 9/8 equivalents of S_8 were used for these control reactions.

1.4. *Reaction of* S_{12} *and* S_{20} *with 1,3-Dienes (2a and 2b) and norbornene (3)*

Trapping reactions for S_{12} and S_{20} were conducted analogously to those for S_9. All products were identified by comparison with authentic samples derived from independent synthesis.

Allotropes S_{12} (*30*) and S_{20} are very poorly soluble in CS_2. Because of this characteristic, the experimental protocol was modified, and each of S_{12} and S_{20} was directly added to the refluxing olefin under heterogenous conditions. S_{12} and S_{20} suspensions were observed to be of fine particle size and trapping yields were reproducible. It should be noted that due to the absence of CS_2 in the reaction media, which in the case of S_9 was used to solubilize the allotrope, no boiling point depression occurs, and reactions proceed at the boiling points of the respective solvents.

Table 4. Reaction of selected olefins with S_9.

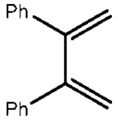
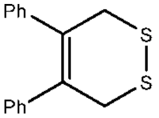
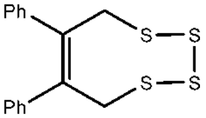
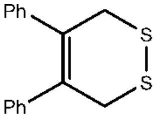
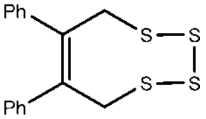
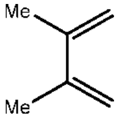
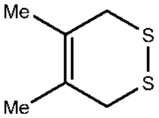
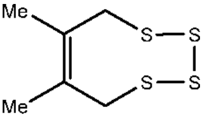
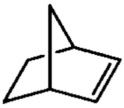
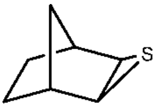
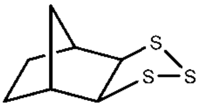
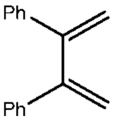
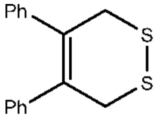
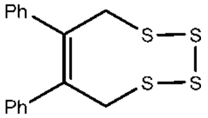
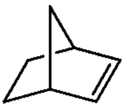
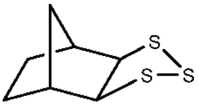
Substrate	Conditions (solvent/temperature/time)	Product ratios and yields	
2a 	Chlorobenzene 115°C; 3 h	  **4a** 6.5:1 **5a**	45%
	Toluene 100°C; 3 h	  **4a** 5.5:1 **5a**	31%
2b 	Toluene 100°C; 3 h	  **4b** 10:1 **5b**	39%
3 	Toluene 100°C; 3 h	  **6** 1.5:1 **7**	26%

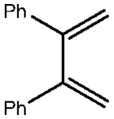
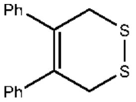
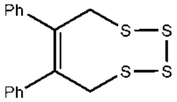
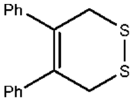
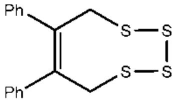
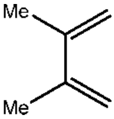
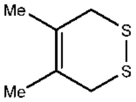
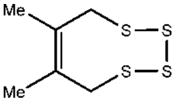
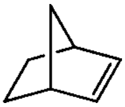
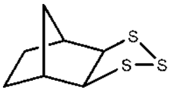
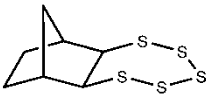
Table 5. Control reactions for S_9 trapping: trapping with S_8.

Substrate	Conditions (solvent/temperature/time)	Product ratios and yields	
2a 	Chlorobenzene 115°C; 3 h	  **4a** 4:1 **5a**	4%
3 	Toluene 100°C; 3 h	 **7**	0%

For both reaction sets, heating was maintained until no more particles could be seen in suspension in the reaction mixture and that either S_{12} or S_{20} had been fully consumed as verified by the HPLC analysis. The results for the reaction between equimolar amounts of S_{12} or S_{20} and 2,3-diphenyl-1,3-butadiene (**2a**), 2,3-dimethyl-1,3-butadiene (**2b**) and norbornene (**3**) are reported in Tables 6 and 7, respectively.

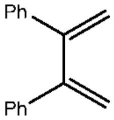
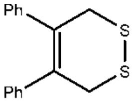
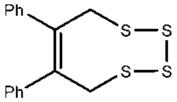
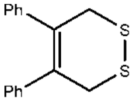
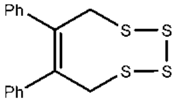
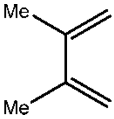
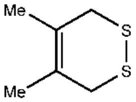
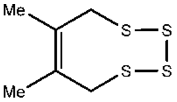
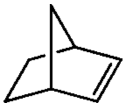
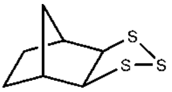
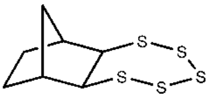
Tables 8 and 9 summarize the results obtained for selected control reactions for S_{12} and S_{20}, respectively. These control reactions were carried out with S_8 as the sulfurating agent with 3/2

Table 6. Reaction of selected olefins with S_{12}.

Substrate	Conditions (solvent/temperature/time)	Product ratios and yields			
2a 	Chlorobenzene 130°C; 3 h	 **4a**	3.5:1	 **5a**	51%
	Toluene 115°C; 15 h	 **4a**	5.5:1	 **5a**	65%
2b 	Toluene 115°C; 15 h	 **4b**	5.5:1	 **5b**	50%
3 	Toluene 115°C; 15 h	 **7**		 **8**	80%[a]

Trace amounts (ca. 4%) of **8** were also detected.

Table 7. Reaction of selected olefins with S_{20}.

Substrate	Conditions (solvent/temperature/time)	Product ratios and yields			
2a 	Chlorobenzene 130°C; 3 h	 **4a**	4.5:1	 **5a**	51%
	Toluene 115°C; 15 h	 **4a**	5.5:1	 **5a**	67%
2b 	Toluene 115°C; 15 h	 **4b**	7.5:1	 **5b**	64%
3 	Toluene 115°C; 15 h	 **7**		 **8**	70%[a]

Trace amounts (ca. 1%) of **8** were also detected.

Table 8. Control reactions for S_{12} trapping: trapping with S_8.

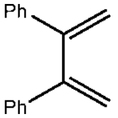
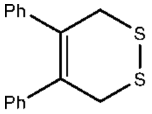
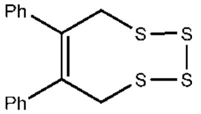
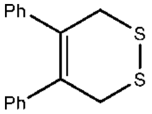
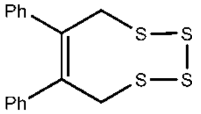
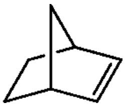
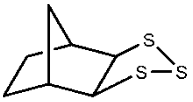
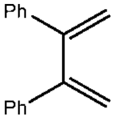
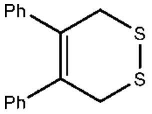
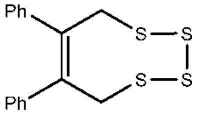
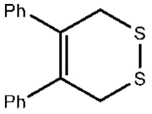
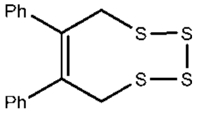
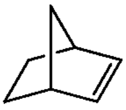
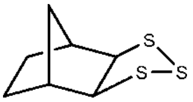
Substrate	Conditions (solvent/temperature/time)	Product ratios and yields	
2a 	Chlorobenzene 130°C; 3 h	 **4a** 7.5:1  **5a**	36%
	Toluene 115°C; 15 h	 **4a** 7:1  **5a**	30%
3 	Toluene 115°C; 15 h	 **7**	38%

Table 9. Control reactions for S_{20} trapping: trapping with S_8.

Substrate	Conditions (solvent/temperature/time)	Product ratios and yields	
2a 	Chlorobenzene 130°C; 3 h	 **4a** 7:1  **5a**	39%
	Toluene 115°C; 15 h	 **4a** 6:1  **5a**	42%
3 	Toluene 115°C; 15 h	 **7**	36%

and 5/2 equivalents used for S_{12} and S_{20} control reactions, respectively, in order to provide a basis for comparison.

2. Discussion

The reaction between equimolar amounts of S_9 and 1,3-dienes **2a** and **2b** yielded the corresponding well-identified disulfide (**4a** and **4b**) and tetrasulfide (**5a** and **5b**) adducts in moderate yields. The product yields were generally slightly lower than the ones obtained in the sulfuration reactions with S_{10} under similar conditions (*27*). Disulfide to tetrasulfide selectivities were similar to those observed for trapping reactions with S_{10}. Notable is the increased disulfide selectivity (10:1) that S_9 affords when **2b** is the substrate as compared with ca. 7:1 in the corresponding S_{10} sulfuration experiment (*27*).

The control reaction with S_8 (Table 5) and **2a** as the substrate indicates that S_9 (Table 4; 45% for **4a** + **5a**) reacts much more efficiently than S_8. In the latter instance, only 4% of trapped products (**4a** + **5a**) were obtained after 3 h at 115°C in chlorobenzene/CS_2.

Yields of sulfuration products obtained for the reaction between equimolar amounts of norbornene (**3**) and S_9 were more modest than that obtained in the corresponding S_{10} sulfuration reaction (26% *vs.* 85%) (*27*). However, the novelty of this new sulfuration reaction comes from the fact that *exo*-2,3-epithionorbornane (**6**) was obtained as one of the two products, along with almost equimolar amounts of trithiolane **7**. Episulfide **6** was identified within the crude reaction mixture by ^{1}H NMR comparison with an authentic sample, the independent synthesis of which is described below; trithiolane **7** had previously been isolated and characterized by Lesté-Lasserre and Harpp (*27*). The control reaction that was carried out between **3** and S_8 produced neither **6** nor **7**. In fact, activation of S_8 by ammonia is often required for sulfuration to take place (*31, 32*).

The S_9-catalyzed interconversion of **6** yielded traces of **7** (ca. 3%) under similar reaction conditions (3 h; 100 °C in toluene/CS_2), whereas none of **6** was detected for the reverse reaction. Additionally, a pure sample of **7** was thermally stable at the reaction temperatures and could be wholly recovered intact. It thus seems evident that **6** and **7** do not exist in equilibrium but are direct products of the sulfuration of **3** with S_9. Their presence in the reaction mixture is not the consequence of thermal decomposition or further reaction with S_9.

This non-equilibrium between **6** and **7** is analogous to the one observed between **4** and **5** with either S_9 (Table 4) or S_{10}. This reactivity seems to contrast with the S_8 sulfuration reaction of norbornene reported by Bartlett and Ghosh (*32*). They demonstrated that **7** was in equilibrium with pentasulfide **8**. Other accounts of such equilibrium processes have also been reported (*33*). In the present study, **8** was never detected in the reaction medium during the trapping reactions with S_9.

Very few examples have been reported of episulfide formation from direct sulfuration of an olefin with sulfur allotropes. A very closely related example is the irradiation of a mixture of S_8 and **3**. Inoue *et al.* (*34*) were able to isolate both **6** and **7** in 8% and 77%, respectively. The authors proposed that **6** formed from the reaction of a photo-excited state of **7** with **3**. This example contrasts strongly with the analogous thermal sulfuration of norbornene, in which case **6** was not detected (*31, 32, 35*). The dearth of examples in the area of episulfide formation by direct sulfuration of olefins by sulfur serves to highlight further the unique behaviour of S_9 toward norbornene.

The reaction of equimolar amounts of S_{12} and S_{20} with 1,3-dienes **2a** and **2b** yielded the expected disulfide and tetrasulfide adducts (Tables 6 and 7). Product distribution was unremarkable compared with the products obtained with S_8, S_9 (vide infra) or S_{10}. Overall yields of trapped products appeared to be almost identical in the case of **2a** with both allotropes (51% at 130°C and ca. 66% at 115°C). In the case where **2b** was the trapping agent, S_{20} sulfurated it more efficiently than S_{12} and with greater selectivity for the formation of **4b**. The overall yields of **4** and **5** are within the range observed in analogous reactions with S_9 or S_{10}. Despite the heterogeneity of the reaction medium, trapping reactions proceeded efficiently. Both S_{12} and S_{20} remained as fine particulate suspensions in the solution, which, contrary to what was observed with S_{10} (*27*), explains why yields were reproducible in the present case.

The mole equivalents are greater in the case of S_{12} and S_{20} when compared with S_9/S_{10} (the active species are likely sulfur radical intermediates, but mechanistic work has not yet been done). The trapping reaction of **2a** with two equivalents of S_{10} resulted in a higher overall yield of **4a** and

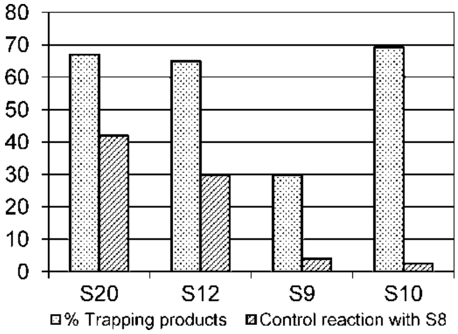


Figure 3. Sulfuration of 2,3-diphenyl-1,3-butadiene (**2b**): comparison of S_9, S_{10}, S_{12} and S_{20}.

5a (86% at 115°C in chlorobenzene/CS_2 for 2.5 h), compared with when a single equivalent of S_{20} was employed (67% at 115°C in toluene for 15 h). When compared with the results obtained by their respective control reactions (Tables 8 and 9) with elemental sulfur (S_8), S_{12} and S_{20} actually appear to be quite poor sulfurating agents towards 1,3-dienes.

Figure 3 summarizes the yield increase obtained with the different sulfur allotropes in this study compared with their respective control reaction yields with S_8 during the small-scale sulfuration reaction with **2a**. Temperatures were 15°C greater for the larger two sulfur allotropes, but reaction times varied widely, ranging from 2 to 3 h for S_{10} and S_9 and up to 15 h for S_{12} and S_{20}. The reaction time depends on how quickly the sulfur ring decomposes at the temperature of the reaction. It is evident from Figure 3 that there is a large difference in sulfuration efficiency between the different allotropes. Although S_{12} and S_{20} sulfurate **2a** 120% and 60% more than S_8, respectively, S_{10} is much more efficient with an increase in yield of 2700%. This comparison thus demonstrates that within the experimental conditions that were used, S_{10} appears to be 45 times more efficient than S_{20} and 22 times more efficient than S_{12} at sulfurating **2a**. The same calculations for S_9 show that this allotrope is 11 and 5 times more efficient than S_{20} and S_{12}, respectively.

Tables 6 and 7 reveal that during the reaction of S_{12} or S_{20} with **2a**, higher yields of trapped products were obtained when lower temperatures were used; 51% trapping at 130°C and ca. 66% at 115°C. This phenomenon does not seem to be solvent-related as control reactions with S_8 exhibit the expected opposite behaviour: higher yields being obtained at high temperatures (Tables 8 and 9). It should however be mentioned that the value observed for the S_{20} control reaction in chlorobenzene seems abnormally low, which we have attributed to the rapid decomposition of S_{12} and S_{20} at elevated temperatures. Indeed, Steudel had previously shown that both allotropes decompose quite rapidly at 130°C (*9*). Similar to S_{10} or S_9, S_{12} and S_{20} rings open to form polymeric sulfur (S_μ), which fractionates upon further heating to ultimately yield S_8. Thus, S_{12} and S_{20} polymerization processes compete with the trapping reaction itself, which serve to explain the observed decreased yields at this temperature. Polymeric sulfur (S_μ) was shown to be completely unreactive toward 1,3-dienes at these temperatures (*36*). When the trapping reactions occur at 115°C, however, the decomposition of both S_{12} and S_{20} is slower, and sulfur trapping can thus more efficiently occur.

In terms of the ratios of disulfide/tetrasulfide adducts, the case of S_{12} is of particular interest. Sulfuration of **2a** and **2b** with S_{12} consistently produced tetrasulfide adducts **5a** and **5b** in larger amounts than what was observed for S_{10}, S_8 and S_9. Ratios of ca. 5.5:1 of disulfide/tetrasulfide were obtained at 115°C for both 1,3-dienes **2a** and **2b**, which contrasts strongly with the maximum 9.5:1 ratio observed with S_{10} (*27*) and the 7:1 ratio observed with S_8 (Table 8). This trend is even more dramatic at higher reaction temperatures. The ratio **4a**:**5a** dropped to as low as 3.5:1 at 130°C (Table 6). The product ratio remained constant at this elevated temperature for both S_{10}

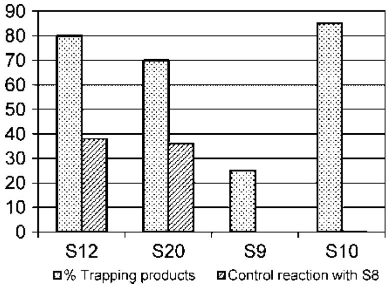


Figure 4. Sulfuration of norbornene (**3**): comparison of S_9, S_{10}, S_{12} and S_{20}.

and S_8 and in fact even increased for S_9 (Table 4). A quick decomposition of S_{12} thus seems to result in an increased tetrasulfide selectivity contrary to what was earlier posited (*37*).

In the case of S_{20}, the results obtained for the ratios of disulfide/tetrasulfide were less straight forward. Although some of these results indicate a similar pattern of behaviour to that observed for S_{12}, a general trend in selectivity cannot be conclusively established. It is interesting to note that in the control reactions for both S_{12} and S_{20}, S_8 trapping by **2a** was revealed to be much more selective for **4a** in both pure chlorobenzene and toluene (Tables 8 and 9) than when the same reaction was conducted in mixed solvent systems as was the case for the S_9 control reactions (Table 5). Thus in our study, reaction temperature cannot be completely deconvoluted from solvent identity when it comes to reaction selectivity.

The reaction between equimolar amounts of S_{12} or S_{20} with norbornene proceeded at 115°C in good overall yields (80% for S_{12} and 70% for S_{20}, cf. Tables 6 and 7). Trithiolane **7** was identified as the major product in both cases. Similar to what was obtained for 1,3-dienes, the sulfuration efficiency of these two allotropes does not appear to be as high as that for S_{10} (*27*). Remarkably, control reactions with S_8 under similar experimental conditions also produced significant amounts of **7** (ca. 37%; cf. Tables 8 and 9). The results obtained are in stark contrast to those observed with S_9, wherein the reaction was essentially arrested. Thus, it would seem that the decrease in temperature from 115°C to 100°C, shorter reaction times (15 h *vs.* 3 h) coupled with CS_2 in the reaction mixture are sufficient changes to shut down sulfuration of **3** with S_8. Figure 4 compares the reactivity of **3** toward each of the S_{12}, S_{20}, S_{10} and S_9 allotropes and references these with respect to their respective control reactions with S_8.

Relatively low (110% and 95%) yield increases were observed when either S_{12} or S_{20} were used as the sulfurating agent instead of S_8. Overall, S_{10} appears to be the most efficient, and this reaction has the added benefit of being milder and faster.

Unlike S_9, which afforded episulfide **6** as the major product of the trapping reaction with **3**, S_{12} and S_{20} produce primarily **7** with trace quantities of highly chalcogenated pentasulfide **8**; control reactions with S_8 did not produce **8** under these non-polar conditions, which differ from what was observed by Bartlett and Ghosh in polar solvents (*32*). This result seems to indicate the ability of S_{12} and S_{20} to liberate longer polysulfide chains than the other sulfur allotropes.

3. Conclusion

The results obtained have demonstrated that in terms of yields, S_9, S_{12} and S_{20} are not as effective sulfurating agents as S_{10} when trapped with 2,3-diphenyl-1,3-butadiene (**2a**), 2,3-dimethyl-1,3-butadiene (**2b**) or norbornene (**3**). These allotropes are more rare and difficult to synthesize than S_{10}, which makes them less appealing and useful for methodology purposes.

However, they have revealed interesting properties with regards to the qualitative results that were obtained. S_9 has the ability to deliver a single sulfur atom equivalent to norbornene. On the other hand, S_{12} and, to a lesser extent, S_{20} show an increased selectivity toward the production of tetrasulfide adducts when reacted with 1,3-dienes **2a** or **2b**. More generally put, these latter sulfur allotropes exhibit an ability to deliver longer polysulfide chains.

4. EXPERIMENTAL

4.1. *General procedures*

The commercially available reagents were obtained from Aldrich Chemical Company. They were used directly without further purification or purified as indicated. Titanocene pentasulfide (**1**) (*38*) and N, N'-dithio-*bis*-phthalimide (*28*) were synthesized as previously described.

Pure sulfur dichloride (SCl_2) was obtained by double flame distillation of technical grade SCl_2 (90%) on phosphorus pentachloride (PCl_5) according to the procedure of Fieser and Fieser (*39*). The red fraction boiling at 58–60°C was collected and used straight away. Sulfuryl chloride (SO_2Cl_2) was distilled and used immediately. The fraction boiling at 68–70°C was collected.

Carbon disulfide (CS_2) used in the reactions involving sulfur allotropes was HPLC grade. The use of HPLC grade CS_2 avoided having to distill this very flammable and toxic solvent. Chlorobenzene and toluene were dried over 4 Å molecular sieves. Methylene chloride (CH_2Cl_2) was rigorously dried by distillation from phosphorus pentoxide (P_2O_5). Tetrahydrofuran (THF) was distilled from the blue sodium- or potassium-benzophenone ketal. Anhydrous diethyl ether ($C_2H_5OC_2H_5$) was stored over 3 Å molecular sieves.

Thin layer chromatography (TLC) was performed on 0.25 mm Merck silica plates (60F-254) with polyester backing and visualized under UV light and/or by dipping into a solution of ammonium molybdate ($(NH_4)_6Mo_7O_{24} \bullet 4H_2O$) (10 g) and ceric ammonium sulfate ($(NH_4)_4Ce(SO_4)_4$) (4 g) in 10% v/v aqueous sulfuric acid (H_2SO_4) (400 mL). Column chromatography was carried out using Silicycle silica gel 60F-254 (230–400 mesh). Flash column chromatography conditions were used in most cases (*40*).

^{1}H NMR spectra were recorded at 200 MHz on Varian XL-200, Varian Gemini-200 or Varian Mercury-200 spectrometers, or at 300 MHz on Varian XL-300 or Varian Mercury-300 spectrometers. ^{13}C NMR spectra were obtained on the same instruments at 50.3 MHz or 75.4 MHz. Deuterated chloroform ($CDCl_3$) was used as a solvent to record these spectra in most cases unless otherwise indicated. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million, δ (ppm) relative to tetramethylsilane (TMS) or to the NMR solvent peak as a reference. The spectra are reported as: shift, multiplicity and integration, respectively. The following abbreviations are used for the multiplicity assignments: ‘s’ for singlet, ‘d’ for doublet, ‘t’ for triplet, ‘q’ for quartet, ‘m’ for multiplet and ‘b’ for broad. The yields of products for the small-scale reactions between various sulfur allotropes (S_9, S_{12} and S_{20}) and 1,3-dienes or simple alkenes were estimated by comparison with an internal standard in 9-methylanthracene. The ^{1}H NMR spectra were recorded with a relaxation delay (d_1) of 5 s at the end of the pulse sequence to ensure accurate integration for the different protons and thus a better estimate on the yields.

MP were recorded on Gallenkamp K 8500 melting point apparatus using open end capillaries and are uncorrected.

Low-resolution electron impact (EI), chemical ionization (CI) or fast atom bombardment (FAB) mass spectra were recorded using a Kratos MS 25RFA instrument equipped with a 70 eV ionizing energy source at McGill University.

The FT-Raman spectra were recorded on a Bruker Model IFS-88 spectrometer with the aid of a Bruker FRA-106 Raman module equipped with an air cooled, 300 mW Nd:YAG laser operating in the near IR region at 1064 nm. The laser did not seem to affect the quality of the sulfur allotrope samples during the acquisition times that were needed in order to get a spectrum. No decomposition was observed even at high laser power. Data are reported in wavenumbers (cm^{-1}). Some intensity of the Raman bands are reported as follows: w, weak; vw, very weak; m, medium; s, strong; vs, very strong; sh, shoulder.

HPLC was performed on an Helwet Packard 1100 Series instrument operated with an HP ChemStation module. The column used for the separation of sulfur allotropes was an HP Hypersil BDS-C18 reverse phase column with a particle size of 5 μm. The internal diameter of the column was 4.6 mm for a total length of 25 mm.

All air sensitive reactions were carried out under an inert nitrogen (N_2) atmosphere. For all water sensitive reactions, the glassware was either previously dried overnight in an oven at 140°C and cooled down in a dessicator containing Drierite or flame dried and cooled under a nitrogen stream. The glassware used for the synthesis of all sulfur allotropes as well as for their trapping reactions with 1,3-dienes or simple olefins was previously left for a few hours in a ca. 1 M hydrochloric acid (HCl) bath. It was then rinsed under water and dried in an oven as described above.

4.2. *Synthesis of S_9*

Pure titanocene pentasulfide (**1**) (3.7 g, 10.9 mmol) was dissolved in 130 mL of HPLC grade CS_2 and cooled down to 0°C over 0.5 h under a nitrogen atmosphere and in the dark. A solution of S_4Cl_2 (2.18 g, 11.0 mmol) in 20 mL of HPLC grade CS_2 was then added dropwise under nitrogen within 20 min via cannulation. The solution was further stirred for 0.5 h in the dark at 0°C under nitrogen. The mixture was then placed in the freezer at −40°C for 4–5 h in order to ensure complete precipitation of Cp_2TiCl_2. The filtrate obtained upon Buchner filtration was concentrated to ca. 30 mL and again placed in the freezer at −40°C overnight in order to precipitate any residual Cp_2TiCl_2. The supernatant was pipetted into a 125 mL Erlenmeyer flask and ca. 19 mL of diethyl ether was added. The flask was left in the freezer at −40°C overnight. Some polymeric sulfur precipitated out, the filtrate was pipetted out, another ca. 19 mL of diethyl ether was added and the solution was kept at −40°C for another 2 days. A precipitate of crude S_9 (826 mg, 26%) formed and upon recrystallization in CS_2/pentane afforded pure S_9 (672 mg, 21%) as bright yellow crystals, MP 61–63°C (*4*, 63–65°C).

4.3. *Synthesis of S_{12} and S_{20}*

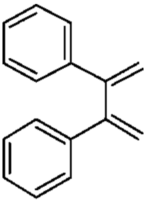
Both S_{12} and S_{20} were obtained as side products of the synthesis of S_6 and S_{10}, respectively, from **1**. These procedures have been described elsewhere (*27, 36*).

4.4. *Extraction of S_{12} from sulfur melts*

The procedure generally followed that of Steudel and Mäusle (*14*). S_8 (400.0 g, 1.56 mol) was placed in a 500 mL beaker and heated for 5–10 min in an oil bath at ca. 200°C. The sulfur melt was then allowed to cool to 140°C within 15 min before being quenched in 2 L of liquid nitrogen. The solid residue was then extracted with 250 mL of CS_2 for 1 h at room temperature. The extracts were then placed in the freezer at −40°C for 1 day and then rapidly filtered on a Buchner funnel. The precipitate of S_8 and $S_{12} \bullet CS_2$ was warmed to room temperature, vigorously shaken with 50 mL of CS_2 and the solution rapidly decanted off; the suspended colourless powdery $S_{12} \bullet CS_2$ was thus carried over with the solution and separated from the large S_8 crystals. The $S_{12} \bullet CS_2$ complex was recovered by filtration on a Buchner funnel and the filtrate returned to the Erlenmeyer containing the remaining $S_8/S_{12} \bullet CS_2$. The extraction procedure was repeated three times.

The crude product was dissolved in 250 mL of CS_2 and placed in the freezer at −40°C overnight. Filtration and prolonged drying on a Buchner funnel afforded 320 mg (0.08%) of S_{12} as a pale yellow solid, MP 145–147°C (*14*, 146–148°C).

4.5. *Synthesis of 2,3-diphenyl-1,3-butadiene (2a)*



2a

Magnesium turnings (1.465 g, 60.3 mmol) were added to a 100 mL three-neck round bottom flask that had been previously flame dried and allowed to cool under a nitrogen stream. Anhydrous diethyl ether (30 mL) was added to the flask and vigorously stirred. A reflux condenser and a flame-dried addition funnel were connected to the flask, and α-bromostyrene (7.9 mL, 90%, 54.6 mmol) was added to the addition funnel. A few drops of α-bromostyrene were added to the magnesium turnings until the reaction was initiated and reflux spontaneously started. Occasionally, the magnesium turnings were crushed with a glass rod in order to reveal new reactive surfaces of magnesium. The remaining α-bromostyrene was diluted with an extra 10 mL of anhydrous diethyl ether and the dropwise addition of the solution completed. Reflux was then maintained for 1 h upon completion of the addition. The mixture was allowed to cool down to room temperature. Grignard reagent was added via a double-ended needle under nitrogen to a 500 mL round bottom flask containing a vigorously stirred solution of dichlorobis(triphenylphosphine)nickel(II) ($(PPh_3)_2NiCl_2$) (3.59 g, 5.49 mmol) and a-bromostyrene (6.3 mL, 90%, 43.7 mmol) in 50 mL of anhydrous diethyl ether at 0°C. The mixture was stirred at 0°C for 30 min, warmed to room temperature and stirred overnight. The mixture was then cooled again on ice, and 150 mL of a 1.2 M HCl solution was added very slowly. The organic phase was separated from the aqueous phase in a separatory funnel and the aqueous phase was further extracted with 4 × 50 mL of diethyl ether. The combined organic extracts were washed with a saturated sodium bicarbonate ($NaHCO_3$) solution (50 mL) and dried over magnesium sulfate ($MgSO_4$). The solvent was evaporated under reduced pressure with a rotary evaporator and an amber oil was produced. The crude product was purified by elution with hexanes on a silica gel flash column chromatography. It afforded pure **2a** (4.51 g) as a waxy white solid in 50% yield.

2a: MP 52–54°C (*41*, 46–47°C) ^1H NMR ($CDCl_3$) δ: 7.2–7.4 (m, 10H), 5.54 (d, 2H), 5.31 (d, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 149.91, 140.25, 128.21, 127.99, 127.55, 116.39 ppm.

4.6. *General procedure for the trapping reaction of S_9, S_{12} and S_{20} with 2,3-diphenyl-1,3-butadiene (2a), 2,3-dimethyl-1,3-butadiene (2b) and norbornene (3)*

Pure olefin **2a**, **2b** or **3** (0.102 mmol) was placed in a three-neck 25 mL round bottom flask and dissolved in 10 mL of chlorobenzene or toluene along with 9-methylanthracene (30.0 mg, 0.156 mmol), the latter of which acts as the internal standard. The mixture was refluxed under a nitrogen atmosphere. Freshly recrystallized S_9 (30.3 mg, 0.105 mmol) was dissolved in CS_2 and the solution concentrated to ca. 500 μL on a warm sand bath. The S_9/CS_2 solution was then injected on top of the hot olefin solution with a syringe over ca. 30 sec. An extra 100 μL of CS_2 was used to rinse the flask that contained S_9 and was subsequently added to the solution. In the case of S_{12} (40.4 mg, 0.105 mmol) and S_{20} (67.3 mg, 0.105 mmol), their low solubility in CS_2 did not allow for their addition as a homogenous solution, and they were simply combined with the olefin prior to heating. Reflux was maintained for 3–15 h. The solution was sampled at desired times and solvent evaporated under reduced pressure with a rotary evaporator. Yields of the expected products were estimated by ^{1}H NMR comparison with the internal standard.

4a: ^{1}H NMR ($CDCl_3$)δ: 6.96–7.12 (m, 10H), 3.67 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$)δ: 142.50, 134.67, 129.19, 127.89, 126.57, 34.59 ppm.

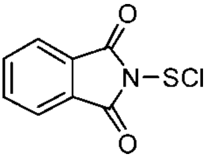
5a: ^{1}H NMR ($CDCl_3$)δ: 7.06–7.14 (m, 10H), 4.07 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$)δ: 140.90, 138.03, 129.55, 128.02, 127.72, 126.97, 126.88, 42.95.

4b: ^{1}H NMR ($CDCl_3$)δ: 3.18 (s, 4H), 1.73 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$)δ: 124.50, 34.62, 21.43 ppm.

5b: ^{1}H NMR ($CDCl_3$)δ: 3.62 (s, 4H), 1.77 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$)δ: 129.59, 43.14, 18.76 ppm.

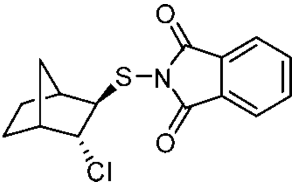
7: ^{1}H NMR ($CDCl_3$)δ: 3.61 (d, $J = 2.0$ Hz, 2H), 2.43 (m, 2H), 1.89 (dt, $J_1 = 10.0$ Hz, $J_2 = 2.0$ Hz, 1H), 1.70 (m, 2H), 1.24 (m, 2H), 1.03 (dt, $J_1 = 10.0$ Hz, $J_2 = 2.0$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$)δ: 69.68, 40.66, 32.21, 27.49 ppm. MS (EI, 70 eV, 100°C) m/z (relative intensity): 190 ($M^{+\cdot}$) (100), 126 (46), 125 (31), 98 (19), 97 (35), 93 (60), 92(24), 91 (45), 79 (26), 77 (31), 67 (21), 66 (65), 65 (24), 64 (28).

4.7. *Synthesis of phthalimido-N-sulfenyl chloride*



N, *N*′-Dithio-*bis*(phthalimide) (20.0 g, 56.1 mmol) was dissolved in 130 mL of $CHCl_3$ in a three-neck 250 mL round bottom flask equipped with a reflux condenser and the temperature was maintained at 50–60°C with an oil bath. Chlorine gas was bubbled through the mixture for 2 h after which the reaction became completely homogeneous. The third neck of the flask was connected to a series of two consecutive bubbling bottles filled with a 1 M KOH solution and water, respectively, in order to ensure complete neutralization of unreacted chlorine gas. After completion of the reaction, nitrogen gas was passed through the reaction mixture for 15 min in order to remove excess Cl_2 (g). The $CHCl_3$ was evaporated, the solid residue filtered on Buchner, washed with some petroleum ether and dried for 5 min. This gave 21.6 g (90%) of phthalimido-*N*-sulfenyl chloride as a yellow solid. This material was stored in the freezer at −40°C; MP 115–116°C (*29*, 115–117°C).

4.8. *Synthesis of endo-3-chloro-exo-2-(phthalimido-N-thio)bicyclo [2.2.1] heptane*

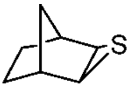


To a solution of norbornene (**3**) (533.0 mg, 5.7 mmol) in 10 mL of dry CH_2Cl_2 under nitrogen was added dropwise a yellow solution of phthalimido-*N*-sulfenyl chloride (1.0 g, 4.7 mmol) in

3 mL of dry CH_2Cl_2 via a cannula. The mixture was subsequently stirred under nitrogen for 12 h. Evaporation of the solvent under reduced pressure gave the desired adduct in quantitative yield.

MP 109–111°C (*29*, 113°C). ^{1}H NMR ($CDCl_3$)δ: 7.7–8.0 (m, 4H), 4.22 (m, 1H), 3.17 (m, 1H), 2.48 (m, 1H), 2.47 (m, 1H), 1.20–1.92 (m, 6H) ppm.

4.9. *Synthesis of exo-2,3-epithionorbornane (6)*



6

Lithium aluminum hydride (252.0 mg, 6.6 mmol) was combined with 10 mL of dry THF in a 50 mL dry round bottom flask. The suspension was stirred under a nitrogen atmosphere and cooled to −78°C for 30 min. A solution *endo*-3-chloro-*exo*-2-(phthalimido-*N*-thio)bicyclo[*2.2.1*] heptane (1.07 g, 3.5 mmol) in 5 mL of dry THF was then added dropwise to the mixture under nitrogen via a double-ended needle over 15 min. The mixture was then stirred for a further 15 min at −78°C before being slowly warmed back to RT. The reaction mixture was then quenched by successive dropwise addition of 250 μL of water, 250 μL of a 15% KOH solution and 3 × 250 μL of water (*42*). The white granular aluminum oxide precipitate that formed upon stirring was collected on a Buchner funnel, the solution dried over $MgSO_4$ and the solvent evaporated. Column chromatography of the residue in 10% $CHCl_3$/hexanes afforded 225 mg (51%) of *exo*-2,3-epithionorbornane (**6**) as a colourless smelly oil.

6: ^{1}H NMR ($CDCl_3$)δ: 2.68 (s, 2H), 2.39 (bs, 2H), 1.54–1.62 (m, 2H), 1.47 (dt, $J_1 = 10.5$ Hz, $J_2 = 2.4$ Hz, 1H), 1.16–1.23 (m, 2H), 0.60 (d, $J = 9.9$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$)δ: 37.43, 37.22, 27.34, 27.30 ppm.

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