μL) in an NMR tube. The reaction proceeded virtually instantaneously at 22 °C to yield *N*-hydroxy-2-(acetylamino)fluorene (**3**)[24] as monitored by NMR: ($CDCl_3$) δ 2.23 (s, Ac_2O), 2.09 (s, AcOH), 2.14 (s, CH_3CON), 3.94 (s, CH_2) [for aromatic protons see Figure 1, Chart B]; MS (FAB+, glycerol), *m/z* (relative intensity) 240 (69, M + H^+), 224 (100), 223 (55), 196 (9), 181 (50), 180 (26); obsd M + H 240.1080, calcd 240.1025.

2. With *p*-Nitrophenyl Acetate. *p*-Nitrophenyl acetate (8 μmol) in EtOH-d_6 (400 μL) was added to *N*-hydroxy-2-aminofluorene (8 μmol) in the same solvent (400 μL) at 22 °C. Orange-red crystals precipitated, and after 48 h the solid product was isolated and identified as 2,2′-azoxyfluorene:[25] NMR ($CDCl_3$) δ 3.99 (2 H, s, CH_2), 4.03 (2 H, s, CH_2), 7.40 (m), 7.60 (m), 7.86 (m), 8.19 (d), 8.40 (d), 8.52 (s), 8.67 (s); mass spectrum was identical with previously published data.[25]

Acknowledgment. We thank Professor P. Gassman, University of Minnesota, Minneapolis, for providing experimental details of their transesterification procedure for preparation of *N*-hydroxyarylacetamides. We thank Professor Z. Dinya, Kossuth University, Debrecen, Hungary, for assistance on IR and mass spectral measurements.

Registry No. **1**, 53-96-3; **3**, 53-95-2; **4**, 6098-44-8; **5**, 610-53-7; **6**, 51348-06-2; **7**, 110319-04-5; **8**, 110319-05-6; *N*-hydroxy-2-aminofluorene, 53-94-1; *O*-acetylhydroxylamine, 19479-87-9; *p*-nitrophenyl acetate, 830-03-5; 2,4-dinitrofluorobenzene, 70-34-8; 2,4-dinitroanisole, 119-27-7; 2,2′-azoxyfluorene, 15961-88-3.

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(24) Evans, F. E., Miller, D. W. *J. Am. Chem. Soc.* **1983**, *105*, 4863.

(25) Iorio, M. A.; Mazzeo-Farina, A.; Seneca, L.; Boniforti, L. *Biomed. Mass Spectrom.* **1985**, *12*, 30.

Sulfuration of the Norbornene Double Bond

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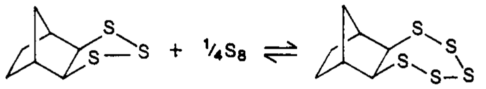
Norbornene reacts with elemental sulfur to give the trithiolane **1** and the pentathiepane **2** in an equilibrium ratio of 3.5:1, the reaction being favored by polar solvents such as dimethylformamide or dimethyl sulfoxide at temperatures as low as 25 °C. Similar sulfuration has been observed with benzonorbornadiene and dicyclopentadiene. Trithiolanes alone are formed in the sulfuration of 2-arylnorbornenes and of benzosesquinorbornenes. The trithiolane from sulfur and isodicyclopentadiene (**9**) is a (2 + 3) adduct derived from the reactive diene tautomer **10**. Norbornadiene is sulfurated to a mixture of five products, including an episulfide, two interbridge disulfides, the "normal" trithiolane, and a 1,6-trisulfide. In all these reactions there is evidence of polar transition states but of no discrete ionic intermediates. The only effect of radical trapping agents is to limit attendant polymerization.

Introduction

The first study of the reaction between norbornene and sulfur was reported in 1969.[1] The only product isolated was the novel *exo*-norbornane trithiolane (**1**), setting norbornene apart from all the acyclic olefins studied in the past. Later Oae and co-workers[2] obtained a similar result by irradiating a solution of norbornene and sulfur. We have extended the study of the sulfur addition[3] to a number of related compounds chosen to reveal the effects of polarity, stereochemistry, double-bond interactions, and solvent on the sulfuration reaction.

Norbornene and Sulfur. Heating a mixture of sulfur and norbornene in dimethylformamide (DMF) or in dimethyl sulfoxide (DMSO) gave two products. The major component could be easily identified as **1** by comparing its NMR and IR spectra with those reported before.[1,2] The minor component could be precipitated as a white solid. A high resolution mass spectral analysis together with a molecular weight determination indicated that five sulfur atoms had added to norbornene. A four-line ^{13}C NMR spectrum showed the molecule to be symmetrical, consistent with the norbornane pentathiepane structure (**2**). In the ^1H NMR spectrum H-2 and H-3 absorb at δ 3.98 and couple with H-7a (w-coupling) with J = 2.0 Hz. It is now accepted[4] that in substituted norbornane systems, an endo proton couples with the anti methylene bridge proton with a coupling constant ca. 2.0 Hz while the exo proton couples with the bridgehead proton with a coupling constant ca. 4.0 Hz, the w-coupling in this case being absent. A characteristic aspect of the ^1H NMR spectra of **1** and **2** is the chemical shift difference of the methylene bridge protons. In **1**, δ(H-7s) − δ(H-7a) = 0.77, whereas in **2**, δ(H-7s) − δ(H-7a) = 0.48. This difference has now been found to exist in all the pairs of trithiolanes and pentathiepanes studied (Table 3, supplementary material).



1 2

In a typical sulfuration reaction the reactants were heated at 100 °C in DMF for 6 h; then the products were worked up by ice-water quenching, precipitation, extraction, and liquid chromatography between 0 °C and room temperature. Combined yields of purified trithiolane and pentathiepane ran around 40%, with the trithiolane–pentathiepane ratio never less than 3:1.

The fact that previous workers[1,2] had not obtained **2** suggested that **2** was decomposing to **1** under the distillation conditions (80 °C/0.05 mm) used. Although $CHCl_3$ and CS_2 solutions of **2** are stable for extended periods, a solution of **2** in DMSO or DMF immediately showed the presence of **1**. ^1H NMR spectra of these solutions showed **1** and **2** to be in the same ratio as obtained in the direct sulfuration of norbornene. By removal of the solvent under vacuum followed by careful preparative TLC it is possible

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(1) Shields, T. C.; Kurtz, A. N. *J. Am. Chem. Soc.* **1969**, *91*, 5415.

(2) Inoue, S.; Tezuka, T.; Oae, S. *Phosphorus Sulfur* **1979**, *4*, 219.

(3) Ghosh, T. Ph.D. Dissertation, Texas Christian University, 1986.

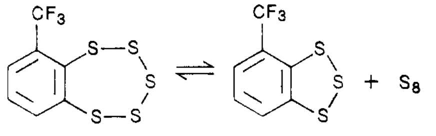
(4) Marchand, A. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie Int.: Deerfield Beach, FL, 1982, pp 174–206.

0022-3263/87/1952-4937$01.50/0

to isolate **1** and **2**, as well as sulfur, from the mixture. The amount of sulfur obtained was in good agreement with the calculated amount based on a **1**:**2** ratio of 3.5:1.

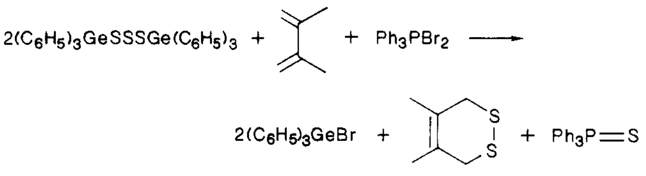
The equilibrium of pentathiepane with trithiolane and sulfur in DMSO is readily established at 25 °C in the forward direction, but only very slowly starting with the trithiolane and sulfur. This was shown to be the result of low solubility of elemental sulfur in DMSO (at 25 °C only 0.097 g of sulfur dissolves in 100 g of DMSO). By using the more soluble S_7NH with the trithiolane in DMSO the same trithiolane:pentathiepane ratio of 3.5 was obtained on overnight stirring as in the runs starting with the pentathiepane.

A similar equilibrium has recently been reported for a benzopentathiepane–trithiolane system.[5] As with **1** and **2**, the equilibrium is attained more rapidly starting from the pentathiepane side.



3 **4**

One way of explaining the disproportionation might be to assume a unimolecular dissociation of **2** to **1** and S_2, the latter immediately oligomerizing to the stable S_8. Very recently Steliou and co-workers[6a] have generated S_2 by a reaction closely related to the triphenyl phosphite ozonide method for $^1O_2$ and still more recently by the decomposition or a transient dithietane.[6b] The S_2 generated in this way could be efficiently trapped by a diene as a Diels–Alder adduct.

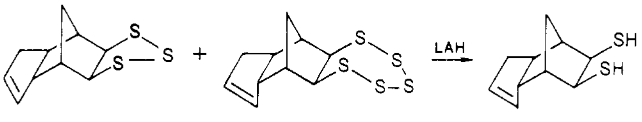


Hence if S_2 is being generated transiently in the decomposition of **2**, a diene might be able to trap it. When a mixture of **2** and 2,3-dimethyl-1,3-butadiene was dissolved in DMSO-d_6 and stirred at 25 °C overnight, NMR analysis revealed that **2** had equilibrated to a mixture of **2** and **1** (ratio 1:3.4) but the diene had remained unchanged.

For more information about the trithiolane–pentathiepane interconversion, a solvent was chosen where the sulfur produced would remain in solution. At 48 °C, mixtures of DMSO and CS_2 are homogeneous when the DMSO content is less than 25% or more than 75% by volume. In the 1:3 solution of DMSO and CS_2 at 48 °C, dissolved pentathiepane was converted into a 68:32 mixture of **1** and **2** in 40 h; in the more polar 3:1 solvent mixture a 66:34 ratio of **1**:**2** was reached in 30 min. The liberated sulfur in each case remained in solution.

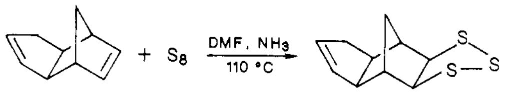
This type of sulfur-ring equilibrium is related to the one recently reported by Tebbe, Wasserman, and co-workers for S_8 and its allotropes S_6 and S_7 at ambient temperatures.[7] Here also it took only a few minutes to detect S_6 and S_7 in solutions of S_8 in methanol, acetonitrile, or DMSO, whereas solutions of S_8 in cyclohexane at room temperature showed little conversion to S_6 or S_7.

Dicyclopentadienes + Sulfur. It has been reported[8] that the reaction of *endo*-dicyclopentadiene with sulfur gives the exo-trithiolane **5** as the only product. When the reaction was repeated (DMF, NH_3, 130 °C, 2 h), NMR analysis of the crude indicated an equal mixture of two components. Thin-layer chromatography over silica gel gave some pure **5** and a second fraction which could not be separated into pure components. The identity of the second product as the pentathiepane **6** rests on the following facts: (a) a high-resolution mass spectrum of the second TLC fraction gave a parent peak with the correct *m*/*e* for the pentathiepane; (b) reduction of the mixture with $LiAlH_4$ gave the single dithiol **7**; (c) when one of the purer samples (90%) of **6** was dissolved in DMSO-d_6 its NMR spectrum immediately indicated equilibration to a 1.4:1 mixture of **5** and **6**; (d) it was possible to assign the ^1H NMR peaks of the **5**:**6** mixture in the way expected if the methylene bridge protons respond to the size of the sulfur ring as in the norbornane trithiolane (**1**) and pentathiepane (**2**).



5 **6** **7**

In contrast to *endo*-dicyclopentadiene, *exo*-dicyclopentadiene under similar reaction conditions underwent sulfuration to give **8** as the only product. Repeated crystallizations gave good quality crystals of **8** (confirmed by X-ray analysis).[9]



8

Isodicyclopentadiene + Sulfur. Although it is known that cycloheptatriene adds sulfur to give the corresponding trithiolane,[10] there are no reports regarding the reactivity of a conjugated diene toward ordinary sulfur.

When a mixture of isodicyclopenta-1-diene (**9**) and 3 equiv of sulfur in DMF was heated to 100 °C after introducing 10–15 bubbles of gaseous ammonia, a single product was obtained in high yield. Both ^{13}C and ^1H NMR spectra indicated the molecule to be unsymmetric and showed the presence of a double bond. The carbons bearing the sulfur atoms were shown to be tertiary from partial decoupling experiments. High resolution mass spectral analysis gave an M^+ consistent with a trithiolane. The only structure consistent with all the NMR characteristics is **11**. It has now been well established that at 100 °C 1-diene **9** undergoes reversible 1,5-sigmatropic shifts to give the more reactive 2-diene **10**.[11] The norbornyl double bond of this diene then undergoes selective sulfuration to give **11**. Following the reaction by ^{13}C NMR with DMF-d_7 as solvent failed to show any transitory adducts of 1-diene and sulfur.

In a recent study of the reactions of tetracyanoethylene (TCNE) with isodicyclopentadiene isomers,[12] it has been

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[5] Chenard, B. L.; Harlow, R. L.; Johnson, A. L.; Vladerchick, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3871.

[6] (a) Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 799. (b) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926.

[7] Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971.

[8] Emsley, J.; Griffiths, D. W.; Jayne, G. J. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 229.

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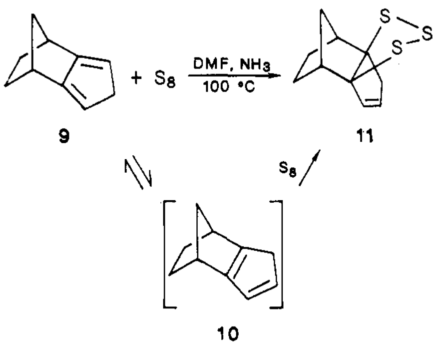
[10] Selms, R. C.; Combs, C. M. *J. Org. Chem.* **1963**, *28*, 2206.

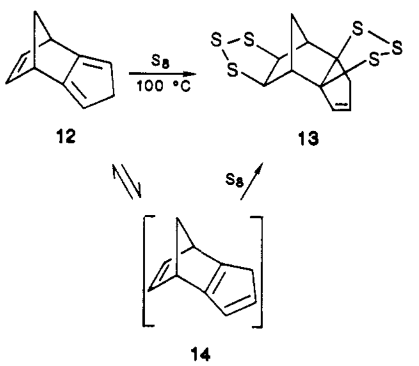
[11] Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

[12] Bartlett, P. D.; Wu, C. *J. Org. Chem.* **1984**, *49*, 1880.

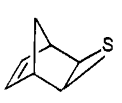


shown that at 0 °C TCNE undergoes a Diels–Alder reaction with **9**, while in refluxing *m*-dichlorobenzene only the adducts of **10** could be obtained. The striking difference between sulfur and TCNE is the exclusive 1,2-addition of the former and 1,4-addition of the latter in reacting with isodicyclopentadiene isomer **10**.

Triene **12** heated with 3 equiv of sulfur gave **13** as the only product in 25% yield. The mass spectrum indicated the incorporation of six sulfur atoms. NMR analysis of the crude reaction mixture did not show the presence of any other compound. Thus it is evident that a symmetrically substituted and an unsubstituted norbornene double bond show the same order of reactivity toward sulfuration.



Norbornadiene. Modes of addition to norbornadiene have been observed which may lead to 2,3-, 2,6-, or 2,7-cycloaddition to the norbornane skeleton.[13-17] With sulfur as the reagent, Emsley and co-workers[8] reported that at 110 °C an episulfide was the only isolable product from norbornadiene. In our work, when norbornadiene was heated with threefold excess of sulfur, five products could be detected by gas chromatography. All of the five components could be separated in relatively pure form as oils by preparative gas chromatography using a 6 ft 5% SE-30 column at 180 °C. Although this method of separation resulted in great loss of material, enough of each product could be collected for a complete spectral analysis. The five products (**15**–**19**) and their spectral data are shown in Table 5 (supplementary material) in order of increasing retention time on a gas chromatography column. The unsaturated episulfide (**15**) has been synthesized by a different route[18] and the ^{1}H NMR chemical shifts are identical with those reported for **15**. The number of sulfur atoms in each compound being known, the symmetry of the norbornane framework was utilized to differentiate between the isomeric sulfides. That **16** is unsymmetrically substituted was evident from its six-line ^{13}C NMR spectrum (actually seven since the absorptions of the two most shielded carbons fall upon each other giving a peak of double intensity) and also the two hydrogens adjacent to the carbons bearing the sulfur chain appear as two multiplets. On the other hand a five-line ^{13}C NMR spectrum coupled with five absorptions in the ^{1}H NMR spectrum is in good agreement with the structure **17**, which possesses a symmetry element. The presence of a cyclopropane moiety is indicated by the two very upfield absorptions (18.01 and 10.02 ppm) in the ^{13}C NMR spectrum. The exo configuration of the trithiolane ring in **18** is reflected by the 2.0-Hz W-coupling between H_2, H_3, and H_{7a}.[19]



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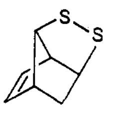

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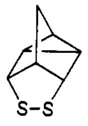

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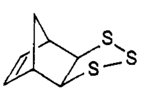

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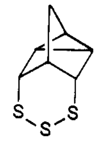

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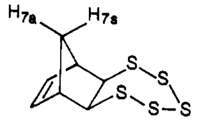
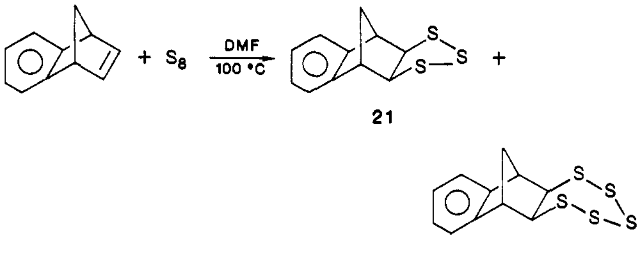


20

The reaction was carried out under different conditions to study the effect of NH_3 catalysis and the effect of 2,6-di-*tert*-butyl-*p*-cresol (BHT), a known free radical interceptor. The relative yields of five products under these different conditions are shown in Table II.

Under the relatively vigorous conditions of reaction between sulfur and norbornadiene, the pentathiepane **20** was not found among the products. However, the cyclic S_7NH is a more active sulfurating agent,[20] and its reaction with norbornadiene at 25 °C yielded about equal amounts of the trithiolane **18** and the pentathiepane **20** with none of the other products seen at higher temperatures. It is thus likely that thermal decomposition of the pentathiepane **20** produces intermediates essential to the formation of the other products **15**–**17** and **19**.

Benzonorbornadiene + Sulfur. Benzonorbornadiene reacts with sulfur under the general condition of sulfuration (no NH_3) to give the trithiolane **21** as the major and the pentathiepane **22** as a minor product. The methylene bridge protons in **21** show a chemical shift difference very similar to those observed for the other trithiolanes in the norbornene series (supplementary material, Table 3). The pentathiepane **22** shows an M^+ at m/e 302 which is the molecular weight of **22**. The chemical shift difference of the methylene protons of **22** compares very well with that obtained for norbornane pentathiepane (**20**). The exo configuration of the sulfur rings in both **21** and **22** is ev-



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(13) Cristol, S. J.; Arganbright, R. P.; Brindell, G. D.; Heitz, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 6035.

(14) Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 1516.

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(16) Cristol, S. J.; Reeder, J. A. *J. Org. Chem.* **1961**, *26*, 2182.

(17) Tanida, H.; Tsuyi, T. *J. Org. Chem.* **1964**, *29*, 849.

(18) Fujisawa, T.; Kobori, T. *Chem. Lett.* **1972**, 1065.

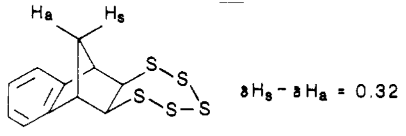
(19) **18** has recently been synthesized by K. Steliou by a different route. Private communication to P. D. Bartlett.

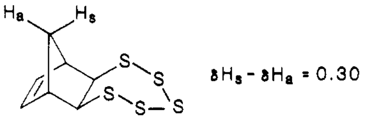
(20) (a) Jenne, H.; Becke-Goehring, M. *Chem. Ber.* **1958**, *91*, 1950. (b) Becke-Goehring, M.; Jenne, H.; Fluck, E. *Chem. Ber.* **1958**, *91*, 1947. (c) Heal, H. G.; Kane, J. *Inorg. Synth.* **1968**, *11*, 184.

Table I. Conditions of Sulfuration

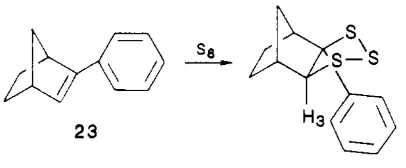
line	substrate	mmol	S source	mmol S	solvent	mL	temp, °C	time, h
1	norbornene	30.8	S_8	90.6	DMF	50	100	6
2	**2**	0.39	**2**	0.76	DMSO	2	25	14
3	2,3-Me_2-butadiene	0.61	**2**	2.55	DMSO-d_6	1.2	25	14
4	*endo*-dicyclopentadiene	3.0	$S_8 + NH_3$	15.6	DMF	10	130	2
5	*exo*-dicyclopentadiene	15.1	$S_8 + NH_3$ (3 mL NH_3)	62.5	DMF	50	110	14
6	**9**	5	S_8	15	DMF + NH_3	20	100	12
7	**12**	2.0	S_8	6.25	DMF	15	120	12
8	norbornadiene	10	S_8	30	DMF	25	96	4
9	norbornadiene	2.0	S_7NH	14	DMF + Me_2NH (200 mg)	15	100	14
10	benzonorbornadiene	2.0	S_8	6	DMF	15	100	14
11	2-phenylnorbornene (**23**)	3	S_8	9.4	DMF + BHT () (0.4 mL)	15	100	12
12	2-*p*-anisylnorbornene	2.0	S_8	16	DMF + 60 mg BHT	10	100	7
13	**28**	0.14	S_8	0.94	DMSO-d_6	0.6	100	7.5

ident from the 2.0-Hz W-coupling observed between the endo protons attached to the carbons bearing the sulfur chain and the anti methylene bridge proton.



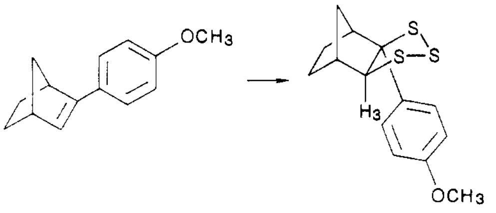


2-Aryl-2-norbornenes + Sulfur. Heating the unsymmetrical 2-phenyl-2-norbornene (**23**) with excess sulfur at 100 °C for 12 h in DMF or DMSO gave the corresponding trithiolane **24** in 24% yield. During TLC of the crude product it was observed that a dark residue remained at the base line. **23** is also a substituted styrene and may undergo polymerization at high temperatures. Thus on the suspicion that competing polymerization was the cause for low yields of the trithiolane the reaction was repeated with 0.1 equiv of 2,6-di-*tert*-butyl-*p*-cresol (BHT) as a free radical captor. This resulted in a significantly increased yield (57%) of **24**. In contrast to the parent norbornene no pentathiepane of **23** could be detected.



23 **24**

Similarly 2-*p*-anisyl-2-norbornene upon treatment with sulfur in the presence of BHT gave the trithiolane **25** in 60% yield. As with **23**, no pentathiepane could be detected.



25

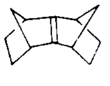
In both the trithiolanes **24** and **25** the configuration of the trithiolane ring was determined by ^1H NMR. The H-3 protons in **24** and **25** absorb at δ 4.00 and 3.95, respectively, and are coupled (W-coupling) to H_{7a} with a coupling constant of 2 Hz.

Table II. Sulfuration of Norbornadiene: Relative Yields of Products under Different Reaction Conditions

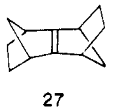
conditions	relative yields, % (by NMR analysis)					
	15	16	17	18	19	20
DMF, 100 °C, 3 h	20	18	14	33	15	
DMF, NH_3, 100 °C, 3 h	15	12	12	57	4	
DMF, BHT (0.2 equiv), 100 °C, 3 h	25	18	15	38	4	
S_7NH, 25 °C				50		50

Both **24** and **25** on gas chromatographic analysis (~150 °C) immediately decompose to the corresponding olefin. This observation has led to some interesting trithiolane transfer chemistry.[21]

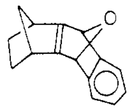
Sulfuration of Sesquinorbornene Double Bonds. Heating **26** with sulfur in DMF or DMSO in the presence or absence of NH_3 for extended periods of time gave no reaction. To test whether steric hindrance to approach of the sulfurating species due to the two methylene bridges and/or the "bumping" of the endo hydrogen atoms on the ethylene bridges was responsible for the inertness of **26**, other *syn*-sesquinorbornene systems were studied.



26



27



28

10-Oxabenzo-*syn*-sesquinorbornene[24] (**28**) is a molecule where due to the oxa bridge the interbridge hindrance on the exo side is greatly reduced. The presence of the fused benzo system eliminates two of the four hydrogen atoms which collide when **26** is saturated.[22,23] Although all *syn*-sesquinorbornenes studied have been shown to possess a nonplanar double bond, **28** has the largest bending yet observed, the dihedral angle being 157.9°, a deviation of 22.1° from the planarity generally associated with carbon–carbon double bonds.

Heating **28** with sulfur in DMSO for 7.0 h gave 40% yield of the trithiolane **29**. Like all other similar adducts of **28**, **29** showed an eight-line ^{13}C NMR spectrum indicating that the symmetry of the sesquinorbornene framework has been retained. An unexpected feature was the chemical shift of the carbons bearing the oxa bridge.

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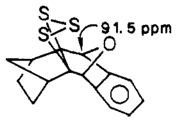
[21] Bartlett, P. D.; Ghosh, T., paper in preparation.

[22] Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984**, *49*, 1875.

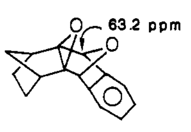
[23] Roof, A. A. M.; Winter, W. J.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 4093.

[24] Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.

In the corresponding epoxide **30**, these carbons absorb at



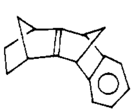
29



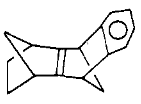
30

63.2 ppm while in **29** the absorption has shifted downfield by ca. 30 ppm. A possible explanation is based on the observation that the chemical shift of the atom next to the carbon bearing the S_3 group is influenced largely by the middle sulfur of the trithiolane ring. From X-ray analysis of some of the norbornane trithiolanes, it has been found that the midle sulfur is oriented away from the methylene bridge.[9,25] Although in **29** the middle sulfur can point in either direction (i.e., toward the CH_2 bridge or toward the oxa bridge), the downfield shift of the carbon bearing the oxa bridge suggests that the sulfur is pointing toward the oxygen. (Is there a donor–acceptor phenomenon existing between the O and S in **29**?) The fact that **28** adds sulfur raises the question whether the substitution of oxygen for a CH_2 is responsible for the enhanced reactivity of **28** in comparison to **26** or is it the absence of the ethylene bridge hydrogens in **28** which allows the molecule to bend more than is possible in **26** to accomodate the S_3 unit?

To differentiate between the two steric factors operating in these systems it was decided to study the sulfuration of **31**, a molecule where both the methylene bridges are present, but due to the incorporation of a benzo group the endo hydrogens are absent in one ethylene bridge. Benzyne cycloaddition to diene **9** gives **31** and the anti isomer **32** in a 3:1 ratio.[24]

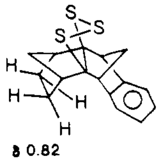


31

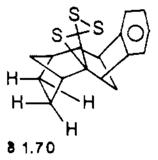


32

Heating a mixture of **31** and **32** with sulfur in DMSO under N_2 (**31** undergoes autoxidation rapidly at room temperature[26]) for 7.0 h gave a mixture of the two trithiolanes **33** and **34** in a ratio of 2.5:1 which could be separated by preparative TLC. In **33** the hydrogens on the ethylene bridge, shielded by the benzene ring, resonate at δ 0.82 whereas in **34**, where this shielding is absent, they resonante at δ 1.70.



33



34

Thus it is evident from the results of sulfuration of sesquinorbornene double bonds that it is the compression of the ethylene bridges toward each other resulting in the "bumping" of the endo hydrogen that is responsible for the intertness of **26** toward sulfuration.

Discussion

Sulfuration of the norbornene double bond appears mechanistically related to interconversions of different cyclic forms of elemental sulfur. Both of these reactions occur at moderate temperatures in a variety of solvents, without any evidence of requiring radical or ionic initiators but with marked facilitation by polar solvents. Sulfuration of the double bond is favored under those same conditions where sulfur is known to enter into equilibrium among a number of ring species and perhaps also viable acyclic fragments S_n. The number and limited characterization of such species continues to delay the precise establishment of any single mechanism for the conversion of norbornene into the trithiolane and pentathiepane and the equilibration between these species.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 197 spectrophotometer. ^1H NMR spectra were obtained on a Varian EM 390 90-MHz spectrometer and a Varian XL 300 300-MHz spectrometer with Me_4Si as internal reference unless otherwise noted. ^{13}C NMR spectra were obtained on JEOL FX-60 and Varian XL-300 spectrometers, operating at 15 and 75 MHz, respectively, with Me_4Si as internal reference. All spectra were obtained in $CDCl_3$ unless otherwise noted. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 2000 using a 25-m capillary column packed with Carbowax 20M, 30 mesh. GC-MS analyses were performed on a Finnigan OWA-1020 GC-MS-DS instrument operating in the EI mode with ionizing energy of 70 eV. The silica gel used for column chromatography separations was 60–200 mesh obtained from Baker Chemical Co. Preparative TLC analyses were performed on 20 × 20 glass plates coated with silica gel (1000 μm) obtained from Analtech, Inc. Elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. High resolution mass spectral analyses were performed by Midwest Center of Mass Spectroscopy, University of Nebraska, Lincoln, NE. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. All reagents and solvents were used as obtained from commercial sources without purification unless otherwise noted. All solvent removal was done under reduced pressure by using a Buchi Rotavapor R110.

Purification of Solvents. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried and distilled by standard methods.[30]

Starting Materials. Substrates for sulfuration, isodicyclopentadiene (**9**),[27] isodicyclopentatriene (**12**),[27] benzonorbornadiene,[28] 2-*p*-anisylnorbornene,[29] 10-oxabenzo-*syn*-sesquinorbornene (**28**),[24] and a mixture of **31** and **32**[24] were prepared by the known methods cited.

Sulfuration Reactions. Table II summarizes the conditions of a number of sulfuration reactions. The workup in all cases was as described here for the sulfuration products of norbornene.

Reaction of Norbornene with Sulfur (Table II, Line 1). A mixture of 2.9 g (30.8 mmol) of norbornene and 2.9 g (90.6 mmol) of sulfur in 50 mL of DMF was heated at 100 °C for 6 h. The reaction was quenched by pouring the reaction mixture into 100 mL of ice-cold water. This was then extracted three times with 30 mL of ether. The ethereal layer was then washed with water and brine and dried over Na_2SO_4. The dark oil (3.0 g) obtained after removal of the ether under reduced pressure was chromatographed over silica gel using pentane/petroleum ether (4:1) as eluant. The light yellow oil obtained after removal of the solvent under reduced pressure was then repeatedly triturated with pentane; 500 mg (2 mmol) of *exo*-3,4,5,6,7-pentathiatricyclo-[7.2.1.0^{2,8}]dodecane (**2**) precipitated out as a white solid. Removal of the pentane from the supernatant liquid gave 1.5 g (9.4 mmol) of *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (**1**) as a light yellow oil.

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[25] Emsley, J.; Griffiths, D. W.; Osborn, R. *Acta Crystallogr., Sect. B* **1929**, *B35*, 2119.

[26] Paquette, L. A.; Bohm, L. C.; Carr, R. V. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 7218.

[27] Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689.

[28] Wittig, G.; Krauss, E. *Chem. Ber.* **1958**, *91*, 895.

[29] Bartlett, P. D.; Webster, E. H.; Dills, C. E.; Richey, H. G. *Ann.* **1958**, *623*, 217.

[30] Furniss, B. B. S.; Hannasord, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; Longman Group, Ltd.: London, 1978; p 277 (DMF) and p 278 (DMSO).

For 1: ^{1}H NMR δ 3.68 (d, J = 2.0 Hz, 2 H), 2.50 (m, 2 H), 1.82 (dt, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1 H), 1.70 (m, 2 H), 1.25 (m, 2 H), 1.05 (dt, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1 H); ^{13}C NMR 69.76 (d), 40.76 (d), 32.29 (t), 27.60 (t) ppm; IR (neat) 2950, 2850, 1440, 1300 cm^{-1}.

For 2: ^{1}H NMR δ 3.93 (d, J = 2.0 Hz, 1 H), 2.43 (m, 2 H), 1.60 (m, 3 H), 1.30 (m, 2 H), 1.12 (dt, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1 H); ^{13}C NMR 75.80 (d), 44.14 (d), 37.74 (t), 28.05 (t) ppm; IR (KBr) 2950, 1440, 1290, 1200, 1140, 1000, 940, 870 cm^{-1}; mp 99–100 °C; mass spectrum, *m/e* calcd for $C_7H_{10}S_5$ 253.9587, obsd 253.9387. Cryoscopic molecular weight, calcd 254, obsd 258.

Disproportionation of Norbornane Pentathiepane (2) (Table II, Line 2). Two bands were obtained which are listed below in order of increasing R_f.

Band 1 (63.7 mg): ^{1}H NMR showed a mixture of 1 and 2 in a ratio of 3.5.

Band 2 (8.1 mg): yellow solid, mp 111–112 °C, showed no depression in mp when mixed with a sample of authentic sulfur.

Disproportionation of 2 in the Presence of 2,3-Dimethyl-1,3-butadiene (Table II, Line 3). To a mixture of 130 mg (0.51 mmol) of 2 and 50 mg (0.61 mmol) of 2,3-dimethyl-1,3-butadiene was added 1.2 mL of DMSO-d_6. The mixture was stirred overnight at room temperature. The mixture remained cloudy. ^{1}H and ^{13}C NMR analysis of the reaction mixture indicated a mixture of **1** and **2** (**1**/**2** = 1.35) and unreacted diene. All the NMR signals obtained from the mixture could be matched with those from pure authentic samples of each component.

Reaction of *endo*-Dicyclopentadiene with Sulfur (Table II, Line 4). Distillation (130 °C/0.02 mm) gave 270 mg (40%) of *exo*-4,5,6-trithiatetracyclo[7.3..1^{2,8}.0^{3,7}]tridec-10-ene (**5**) as a light yellow solid. Sublimation followed by crystallization from ethanol gave light yellow crystals of **5**, mp 70–72 °C: ^{1}H NMR δ 5.74 (m, 1 H), 5.60 (m, 1 H), 3.73 (one half of an AB quartet each split into a doublet, J_{AB} = 7.1 Hz, J = 2.0 Hz, 1 H), 3.68 (other half of the AB quartet each split into a doublet, J_{AB} = 7.1 Hz, J = 2.0 Hz, 1 H), 3.28 (m, 1 H), 2.70 (spt, 1 H), 2.60 (m, 1 H), 2.35 (m, 3 H), 2.10 (d, J = 10.9 Hz, 1 H), 1.30 (d, J = 10.9 Hz, 1 H); ^{13}C NMR 132.10 (d), 130.75 (d), 66.16 (d), 62.64 (d), 57.97 (d), 45.12 (d), 43.71 (d), 40.50 (d), 35.63 (t), 31.64 (t) ppm; IR (KBr) 3020, 2950, 1440, 1260, 1140, 980, 940, 760, 740, 660 cm^{-1}; mass spectrum, *m/e* calcd for $C_{10}H_{12}S_3$ 228.0101, obsd 228.0096.

In a separate experiment 300 mg of the crude, obtained after workup, was subjected to preparative TLC over silica gel using hexane/petroleum ether (7:3) as eluant. Repeated chromatography (since only partial separation was obtained each time) gave a fraction (50 mg) which was found to be 85% pure *exo*-4,5,6,7,8-pentathiatetracyclo[9.3.0.1^{2,10}.0^{3,9}]pentadec-12-ene (**6**): ^{1}H NMR δ 5.80 (m, 1 H), 5.60 (m, 1 H), 4.00 (one half of an AB quartet each split into a doublet, J_{AB} = 7.1 Hz, J = 2.2 Hz, 1 H), 3.90 (other half of the AB quartet each split into a doublet, J_{AB} = 7.1 Hz, J = 2.2 Hz, 1 H), 3.12 (m, 1 H), 2.68 (m, 2 H), 2.30 (m, 3 H), 1.80 (d, J = 10.9 Hz, 1 H), 1.38 (d, J = 10.9 Hz, 1 H); ^{13}C NMR 132.52 (d), 130.92 (d), 72.10 (d), 68.09 (d), 51.76 (d), 47.67 (d), 47.62 (d), 40.69 (d), 38.13 (t), 32.03 (t) ppm; mass spectrum, *m/e* calcd for $C_{10}H_{12}S_5$ 291.9542, obsd 291.9543.

Tricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-dithiol (7) was prepared by adding dropwise 1 mL of a 1 M $LiAlH_4$ solution in ether to 200 mg (0.88 mmol) of **6** dissolved in 15 mL of dry ether under an atmosphere of N_2. The mixture was stirred overnight at room temperature. To the reaction mixture (which now had a white precipitate) was added 25 mL of an ice-cold 5% HCl solution. The ether layer was then separated, washed with water, brine, and dried over $MgSO_4$. Removal of the ether under reduced pressure gave 170 mg (96.5%) of **7** as a light yellow liquid: ^{1}H NMR δ 5.71 (dd, J_1 = 5.8 Hz, J_2 = 2.2 Hz, 1 H), 5.58 (dd, J_1 = 5.8 Hz, J_2 = 2.2 Hz, 1 H), 3.35 (t, J = 6.9 Hz, 1 H), 3.23 (t, J = 6.9 Hz, 1 H), 3.06–3.18 (m, 1 H), 2.58 (spt, J = 3.8 Hz, 1 H), 2.36 (d, J = 4.3 Hz, 1 H), 2.28 (dd, J_1 = 9.4 Hz, J_2 = 2.2 Hz, 1 H), 2.24 (m, 1 H), 2.16 (d, J = 4.3 Hz, 1 H), 2.08 (d, J = 9.9 Hz, 1 H), 1.84 (d, J = 7.1 Hz, 1 H), 1.80 (d, J = 7.1 Hz, 1 H), 1.44 (d, J = 9.9 Hz, 1 H); ^{13}C NMR 131.89, 131.44, 53.15 (2C), 51.07, 43.92, 42.49, 40.80, 35.93, 32.09 ppm; IR (neat) 3050, 2900, 2450 (w), 1440, 1250 cm^{-1}; mass spectrum, *m/e* calcd for $C_{10}H_{14}S_2$ 198.0537, obsd 198.0537.

In a separate experiment a 1:1 mixture (200 mg) of **5** and **6** was reduced with $LiAlH_4$ by using the same procedure as above. After workup 130 mg of a light yellow oil was obtained having ^{1}H and ^{13}C NMR and IR spectra identical with those of **7**.

Preparation of *exo*-4,5,6-Trithiatetracyclo[7.3.1.0.1^{2,8}.0^{3,7}]tridec-10-ene (8) (Table II, Line 4). Sublimation followed by recrystallization from absolute EtOH gave a pale yellow solid (1.4 g, 40%): mp 99–100 °C; ^{1}H NMR δ 5.74 (m, 1 H), 5.46 (m, 1 H), 3.70 (m, 2 H), 2.5–2.80 (m, 2 H), 2.28 (m, 2 H), 2.16 (s, 1 H), 1.98 (d, 1 H), 1.78 (d, J = 12 Hz, 1 H), 1.26 (d, J = 12 Hz, 1 H); ^{13}C NMR 133.2 (d), 130.5 (d), 69.9 (d), 69.4 (d), 54.8 (d), 47.1 (d), 44.9 (d), 42.9 (d), 38.7 (t), 26.2 (t) ppm; IR (KBr) 3050, 2900, 1440, 1300, 1160, 1050, 820 cm^{-1}. Anal. Calcd for $C_{10}H_{12}S_3$: C, 52.6; H, 5.3; S, 42.1. Found: C, 52.1; H, 5.2; S, 42.2.

***exo*-3,4,5-Trithiatetracyclo[5.2.1.0^{2,6}.3^{2,6}]tridec-10-ene (11) (Table II, Line 6).** Kugelrohr distillation (140 °C/0.01 mm) followed by recrystallization from EtOH (absolute) gave 260 mg of pure **11**: mp 137 °C; ^{1}H NMR δ 5.75 (m, 1 H), 5.65 (m, 1 H), 2.95 (td, 1 H), 2.40–2.65 (m, 4 H), 1.15–1.60 (m, 5 H); ^{13}C NMR 132.93 (d), 131.57 (d), 95.77 (s), 85.95 (s), 44.76 (d), 44.11 (t), 43.40 (d), 37.23 (t), 25.20 (t), 22.54 (t) ppm; IR (KBr) 3040, 2900, 1440, 1290, 1130, 940, 780 cm^{-1}; mass spectrum, *m/e* calcd for $C_{10}H_{12}S_3$ 228.0101, obsd 228.0097.

***exo*-4,5,6-*exo*-10,11,12-Hexathiapentacyclo[7.3.3.0.1^{2,8}.-0^{3,7}]hexadec-13-ene (13) (Table II, Line 7).** TLC over silica gel using CH_2Cl_2/EtOAc (7:3) as eluant gave 130 mg of **13** as a pale yellow solid, yield 40%: mp 123–126 °C; ^{1}H NMR δ 5.85 (m, 1 H), 5.70 (m, 1 H), 3.88 (one half of an AB quartet each split into a doublet, J_{AB} = 7.6 Hz, J = 2.2 Hz, 1 H), 3.79 (other half of an AB quartet each split into a doublet, J_{AB} = 7.6 Hz, J = 2.2 Hz, 1 H), 3.10 (dt, J_1 = 18 Hz, J_2 = 2.2 Hz, 1 H), 2.75 (dt, J_1 = 18 Hz, J_2 = 2.2 Hz, 1 H), 2.71 (s, 1 H), 2.65 (s, 1 H), 2.54 (dt, J_1 = 11 Hz, J_2 = 1.5 Hz), 2.36 (td, J_1 = 11 Hz, J_2 = 1.5 Hz, 1 H); ^{13}C NMR 133.43 (d), 131.67 (d), 96.11 (s), 85.12 (s), 66.37 (d), 63.79 (d), 48.82 (d), 47.54 (d), 43.99 (t), 32.04 (t) ppm; IR ($CHCl_3$) 3050, 2900, 1440, 1270, 900 cm^{-1}; mass spectrum, *m/e* calcd for $C_{10}H_{10}S_6$ 321.9107, obsd 321.9111.

Reaction of Norbornadiene with Sulfur (Table II, Line 8). The NMr and mass spectral data of the five fractions obtained are listed in the supplementary material, Table 3.

IR for **16** (neat): 3050, 2950, 1440, 1320, 1260, 800, 730 cm^{-1}.

IR for **17** (neat): 2925, 2850, 1280, 1220, 950, 800 cm^{-1}.

IR for **18** (neat): 3050, 2950, 1440, 1310, 1260, 750 cm^{-1}.

IR for **19** (neat): 2900, 1440, 1280, 1210, 820 cm^{-1}.

All five components were obtained as light yellow liquids which had a tendency to polymerize (becoming relatively insoluble in $CDCl_3$) when kept at room temperature for extended periods of time.

Preparation of S_7NH. S_7NH was prepared by the method of Jenne and Becke-Goehring, with the modifications introduced by Heal and Kane.[20a,c]

Reaction of S_7NH with Norbornadiene (Table II, Line 9). A ^{1}H NMR spectrum of the mixture indicated equal amounts of **18** and **20**. Trituration of this mixture with pentane gave 60 mg of **20** as a white solid. Distillation (100 °C, 3 mm) of the oil, obtained after removal of the pentane, gave 90 mg of **18**. A dark gummy residue in the flask indicated polymerization had taken place during distillation.

For 20: mp 77–80 °C; ^{1}H NMR δ 6.40 (m, 2 H), 3.95 (d, J = 2.0 Hz, 2 H), 2.90 (m, 2 H), 1.86 (d, J = 9.3 Hz, 1 H), 1.56 (dt, J_1 = 9.3 Hz, J_2 = 2.0 Hz, 1 H); ^{13}C NMR 138.61, 70.99, 49.11, 45.08 ppm; IR (CCl_4) 3050, 2950, 1440, 1320, 1240, 700 cm^{-1}; mass spectrum, *m/e* calcd for $C_7H_8S_5$ 251.9229, obsd 251.9223.

Reaction of Sulfur with Benzonorbornadiene (Table II, Line 10). 8,9-Benzo-thiatricyclo[5.2.1.0^{2,6}]decene (**21**) (250 mg) was obtained as a yellow oil: ^{1}H NMR δ 7.23 (m, 2 H), 7.10 (m, 2 H), 3.98 (d, J = 2.0 Hz, 2 H), 3.39 (m, 2 H), 2.70 (d, J = 10.0 Hz, 1 H), 1.95 (dt, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1 H); ^{13}C NMR 146.55, 126.61, 121.62, 70.58, 47.81, 43.56 ppm; IR (neat) 3040, 2950, 1460, 1260, 1150, 1000, 950, 760, 720, 670 cm^{-1}; mass spectrum, *m/e* calcd for $C_{11}H_{10}S_3$ 237.9944, obsd 237.9944. 10,11-benzo-*exo*-3,4,5,6,7-Pentathiatricyclo[7.2.1.0^{2,8}]undecene (**22**) (60 mg) was obtained as a white solid, which was recrystallized by being dissolved in CH_2Cl_2 and adding pentane until dissolved, followed by cooling to −20 °C: mp 115–118 °C; ^{1}H NMR δ 7.23 (m, 2 H), 7.10 (m, 2 H), 4.06 (d, J = 2.0 Hz, 2 H), 3.42 (m, 2 H), 2.18 (d, J = 10.0 Hz, 1 H), 1.87 (dt, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1 H); ^{13}C NMR 145.96, 126.84, 121.70, 72.70, 50.79, 45.90 ppm; IR (CCl_4) 3050, 2950, 1460, 1270, 960 cm^{-1}; mass spectrum, *m/e*

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calcd for $C_{11}H_{10}S_5$ 301.9386, obsd 301.9383. Recently it has been found that trituration of a mixture of **21** and **22** with pentane and chilling at −20 °C gives pure crystalline **22**. Removal of the pentane under reduced pressure gives **21**.

Preparation of 2-Phenyl-*exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (24) (Table II, Line 11). Repetitive trituration with pentane and chilling at −20 °C gave a solid: mp 54–56 °C; ^{1}H NMR δ 5.30 (m, 5 H), 4.00 (d, J = 2.0 Hz, 1 H), 3.20 (s, 1 H), 2.48 (d, J = 10.8 Hz, 1 H), 2.38 (s, 1 H), 1.60 (m, 2 H), 1.40 (m, 1 H), 1.30 (d, J = 10.8 Hz, 1 H), 1.05 (m, 1 H); ^{13}C NMR 143.2 (s), 127.6, 126.8 (3C), 86.9 (s), 69.3 (d), 45.1 (d), 42.1 (d), 33.9 (t), 27.3 (t), 24.4 (t) ppm; IR (neat) 3050, 2950, 2850, 1660–1940 (weak overtones), 1590, 1480, 1460, 1440, 1300, 1160, 1025, 900, 750, 700, 640 cm^{-1}; mass spectrum, m/e calcd for $C_{13}H_{14}S_3$ 266.0257, obsd 266.0249; M_r calcd 266, obsd 264.

Preparation of 2-*p*-Anisyl-*exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (25) (Table II, Line 12). **26** (380 mg, 65%) was isolated as a yellow oil: ^{1}H NMR δ 7.20 (m, 2 H), 6.83 (m, 2 H), 3.95 (d, J = 2.0 Hz, 1 H), 3.80 (s, 3 H), 3.20 (s, 1 H), 2.50 (d, J = 10.8 Hz, 1 H), 2.38 (s, 1 H), 1.30–1.75 (s of m, 3 H), 1.25 (d, J = 10.8 Hz, 1 H), 1.10 (m, 1 H); ^{13}C NMR 158.43 (s), 135.49 (s), 128.36 (d), 115.24 (d), 86.92 (s), 69.46 (d), 55.20 (q), 45.32 (d), 42.19 (d), 34.09 (t), 27.37 (t), 24.40 (t) ppm; IR (neat) 3025, 2950, 1600, 1500, 1450, 1260, 1180, 1030, 900, 820, 740 cm^{-1}; MS (70 eV), M$^+$ not observed, m/e 200 (30%) was observed indicating immediate loss of sulfur followed by a loss of ethylene to give m/e 172 (100%). Anal. Calcd for $C_{14}H_{16}OS_3$: C, 56.8; H, 5.4; S, 32.4. Found: C, 56.8; H, 5.7; S, 32.7.

Preparation of 1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methano-4a,9a-*exo*-trithiaanthracene (29) (Table II, Line 13). Chromatography over silica gel with pentane/Et_2O (65:35) as eluant gave 20 mg of **29** as a viscous oil, yield 46%: ^{1}H NMR δ 7.35 (m, 2 H), 7.20 (m, 2 H), 5.60 (s, 2 H), 3.15 (d, J = 10.4 Hz, 1 H), 2.58 (m, 2 H), 1.25 (m, 2 H), 1.10 (d, J = 10.4 Hz, 1 H), 0.75 (m, 2 H); ^{13}C NMR 147.18 (s), 126.51 (d), 121.90 (d), 91.84 (s), 91.53 (d), 45.75 (t), 46.41 (d), 22.88 (t) ppm; IR (neat) 3005, 2900, 1640, 1450, 1320, 1200, 900, 720 cm^{-1}; mass spectrum, m/e calcd for $C_{15}H_{14}OS_3$ 306.0206, obsd 306.0201.

Preparation of 1,2,3,4,9,10-Hexahydro-1,4-*exo*-methano-9,10-*exo*-methano-4a,9a-*exo*-trithiaanthracene (33) and 1,2,3,4,9,10-Hexahydro-1,4-*exo*-methano-9,10-*endo*-methano-4a,9a-*exo*-trithiaanthracene (34). A mixture of **31** and **32** (200 mg, 1 mmol) (**38**/**39** = 2.0) and 150 mg (4.7 mmol) of sulfur in 8 mL of DMSO was heated at 100 °C under an atmosphere of N_2 for 8 h. The reaction mixture was poured into 20 mL of ice-cold water. This was then extracted twice with 15 mL of ether. The ethereal layer was washed with brine and dried over Na_2SO_4. The crude, obtained after removal of the ether under reduced pressure, was chromatographed over silica gel by using CCl_4/petroleum ether (4:1) as eluant, to give 20 mg of **34** and 50 mg of **33**. Total yield of **33** and **34** was 23%.

For 34 (R_f 0.39): ^{1}H NMR δ 7.00 (m, 2 H), 6.90 (m, 2 H), 3.40 (s, 2 H), 2.80 (d, J = 10.3 Hz, 1 H), 2.70 (s, 2 H), 2.50 (d, J = 11.2 Hz, 1 H), 1.90 (d, J = 11.2 Hz, 1 H), 1.70 (m, 4 H), 1.20 (d, J = 10.3 Hz, 1 H); ^{13}C NMR 147.44, 125.63, 123.70, 89.59, 52.07, 50.63, 47.69, 43.69, 24.43 ppm; IR (CCl_4) 3080, 1450, 1260, 970 cm^{-1}; mass spectrum, m/e calcd for $C_{16}H_{16}S_3$ 304.0414, obsd 304.0413.

For 33 (R_f 0.53): ^{1}H NMR δ 7.20 (m, 2 H), 7.05 (m, 2 H), 3.90 (d, J = 9.8 Hz, 1 H), 3.70 (s, 2 H), 3.25 (d, J = 10.3 Hz, 1 H), 2.70 (s, 2 H), 1.85 (d, J = 9.8 Hz, 1 H), 1.10 (d, J = 10.3 Hz, 1 H), 0.85 (m, 4 H); ^{13}C NMR 148.18, 125.70, 123.10, 93.20, 59.39, 56.63, 49.64, 45.63, 24.65 ppm; IR (neat) 3000, 1450, 1260, 900, 750 cm^{-1}; mass spectrum, calcd for $C_{16}H_{16}S_3$ 304.0414, obsd 304.0417.

Both **33** and **34** when left for extended periods of time at room temperature became glassy solids, insoluble in $CDCl_3$.

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Supplementary Material Available: Tables of ^{1}H NMR chemical shifts in the trithiolanes and pentathiepanes, significant ^{1}H and ^{13}C chemical shifts for **5** and **6**, and NMR and MS data of polysulfides obtained in the sulfuration of norbornadiene (3 pages). Ordering information is given on any current masthead page.

Construction of Five-Membered Rings by Michael Addition–Radical Cyclization

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Enamines react with Michael acceptors **8–10** to produce ketones that, on treatment with lithium acetylides, afford hydroxy acetylenes **3**. These compounds then undergo radical cyclization when treated with triphenyltin hydride and AIBN. The products **6** are formed by 5-exo–digonal closure and furnish substituted cyclopentanones by ozonolysis.

Until recently, most procedures used in synthesis for making carbon–carbon bonds were based on ionic or concerted reactions, and the possibility of using free radicals was not widely recognized—at least outside the area of polymer chemistry.[1] This situation is now changing, and free-radical methods[2] for making carbon–carbon bonds will, undoubtedly, come to occupy an important place in organic synthesis. There already exists extensive modern literature[2,3] on *intermolecular* reactions (e.g., eq 1, A = electron-withdrawing group), and there is a rapidly growing interest[2,4,5] in the synthetic utility of intramolecular cy-

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[1] For early, isolated examples of the synthetic use of radicals to make carbon–carbon bonds, see: (a) Bakuzis, P.; Campos, O. O. S.; Bakuzis, M. L. F. *J. Org. Chem.* **1976**, *41*, 3161. (b) Büchi, G.; Wüest, H. *Ibid.* **1979**, *44*, 546. See also: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386.

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