The Synthesis and Spectra of Polycyclic 1,2,3-Trithiolans

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Polycyclic 1,2,3-trithiolans have been made by reacting the olefins, *exo-* and *endo-*cyclopentadiene dimer, cyclopentadiene trimer, and norbornene with elemental sulphur. The reaction with norbornadiene produced an episulphide. The vibrational (i.r. and Raman) and magnetic (¹H and ¹³C n.m.r.) spectra of the trithiolans are consistent with a five-membered ring structure with three adjacent sulphur atoms in an *exo-*configuration. The trithiolans are chemically fairly stable but polymerise rapidly on heating above 180°C.

ALTHOUGH polycyclic 1,2,3-trithiolans † are reported in several recent patents [1-3] they are only briefly dealt with in the chemical literature.[4,5] Larger rings with three adjacent sulphur atoms such as 1,2,3-trithians and 1,2,3-trithiepins have been recorded.[6-8] The lack of information about trithiolans at present is evident by their complete neglect in the latest comprehensive organosulphur text.[9]

Kurtz and Shields were the first to react norbornene and sulphur and obtain a trithiolan.[4] Polycyclic 1,2,3-trithiolans can better be made from other norbonenes and elemental sulphur activated by amines and 1,3,4-thiadiazoles. Assuming a free radical addition, then the expected products should be *exo,cis*-trithiolans.[10] The four trithiolans discussed in this paper are shown to have properties consistent with this structure, and conclusive proof in the form of an *X*-ray diffraction picture has been published.‡

EXPERIMENTAL

Instruments.—N.m.r. spectra were run on samples in CDCl₃ with Perkin-Elmer R12B (60 MHz) and Bruker HFX90 (90 MHz, ¹H; 22.628 2 MHz, ¹³C broad-band decoupled) spectrometers. I.r. spectra were measured with a Perkin-Elmer 457 spectrometer (CsBr optics) for Nujol and hexachloro-butadiene mulls. Raman spectra were run at Royal Holloway College on a Coderg PHo Raman spectrometer (double monochromator) with a coherent radiation laser operating on the red line (λ 647.1 nm).

Materials.—The olefins were either commercial samples {norbornene (1), norbornadiene (3), *endo*-cyclopentadiene dimer(*tricyclo*[5.2.1.0²,⁶]*dec-3-ene*)(5)} or were synthesised according to published methods (*exo*-cyclopentadiene dimer,[11] cyclopentadiene trimer [12]). The sulphur was reagent grade precipitated sulphur, S₈, from B. D. H.

Reaction of Sulphur and Norbornene.[4]—Sulphur (5.1 g, 0.16 g-atom) was mixed with dimethylformamide (3 cm³) and pyridine (57 cm³) and 'activated' by bubbling NH₃ through the mixture. Norbornene (7.5 g, 0.08 mol) was added and the mixture heated at 110 °C with stirring for 2 h. The mixture was cooled, extracted with ether, and the extract vacuum distilled to yield (2) (3.5 g, 0.018 mol, 34.6%), b.p. 175—180 °C/13 mmHg (Found: C, 44.6; H, 5.3. Calc. for C₇H₁₀S₃: C, 44.2; H, 5.30%); i.r., Raman and n.m.r. spectral data are given in Tables 1—3.

Reaction of Sulphur and Norbornadiene.—Sulphur (5.1 g,

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† Also called 3,4,5-trithiolans.
‡ J. Emsley, D. W. Griffiths, and R. Osborn, *J.C.S. Chem. Comm.*, 1978, 658.

0.16 mol) was mixed with dimethylformamide (3 cm³) and pyridine (57 cm³) and 'activated' by bubbling NH₃ through the mixture. Norbornadiene (7.3 g, 0.08 mol) was added and the mixture heated at 110 °C with stirring for 2 h. The mixture was cooled, extracted with ether, and the extract vacuum distilled to yield a yellow oil, C₇H₈S, (4) (1.9 g, 0.015 mol, 19.3%), b.p. 105—110 °C/13 mmHg (Found: C, 67.5; H, 6.24; S, 24.9. Calc. for C₇H₈S: C, 67.7; H, 6.49; S, 25.8%); δ(SiMe₄) 1.27 (d, 1 H, CH bridge, *J* 9.1 Hz), 1.83 (d, 1 H, CH bridge), 2.95 (tr, 2H, CH bridgehead), 3.02 (s, 2 H, CHS), and 6.37 (tr, 2 H, CH olefinic, *J* 1.7 Hz). I.r. bands centred at 400m, 521w, 640s, 710sh, 720vs, 785m, 801m, 878m, 895sh, 900m, 954m, 967vw, 992m, 1 058m, 1 095w, 1 196m, 1 234m, 1 260m, 1 310s, 1 318s, 1 445s, 1 554w, 1 580w, 1 630w, 2 870w, 2 960m, 3 000s, 3 060m, and 3 120w cm⁻¹. The use of the above method [4] with cyclopentadiene dimer and trimer gave only small yields of trithiolans. It was found necessary to use a stronger sulphur activator and 2,5-bis(octyldithio)-1,3,4-thiadiazole was used.

Reaction of Sulphur and endo-*Cyclopentadiene Dimer.*—Sulphur (10.5 g, 0.33 mol) was added during 20 min to *endo*-cyclopentadiene dimer (44.2 g, 0.34 mol) at 100 °C containing triethylamine (0.5 g) and 2,5-bis(octyldithio)-1,3,4-thiadiazole (0.5 g), as sulphur 'activators'. After the mixture had been heated at 120 °C for 30 min and cooled, the product was extracted with light petroleum (b.p. 40—60 °C) and recrystallised from methanol. This was *endo*-(6) (14.9 g, 0.065 mol, 20%), m.p. 69 °C (Found: C, 52.6; H, 5.35; S, 41.8. Calc. for C₁₀H₁₂S₃: C, 52.6; H, 5.26; S, 42.1%); i.r. and n.m.r. spectral data are given in Tables 1—3.

Reaction of Sulphur and exo-*Cyclopentadiene Dimer.*—In an identical reaction the corresponding *exo*-derivative, *exo*-(6) was prepared, m.p. 101—102 °C (Found: C, 52.2; H, 5.35; S, 41.8); i.r., Raman and n.m.r. spectral data are given in Tables 1—3.

Reaction of Sulphur and Cyclopentadiene Trimer.—Sulphur (1.8 g, 0.056 mol) was slowly added to cyclopentadiene trimer (11.4 g, 0.06 mol) at 100 °C containing triethylamine (0.15 g) and 2,5-bis(octyldithio)-1,3,4-thiadiazole (0.15 g) and the whole kept at 120 °C for 30 min. The mixture was cooled and the product extracted with light petroleum (b.p. 40—60 °C) to give (8) (4.7 g, 0.016 mol, 85%), m.p. 188—190 °C, recrystallized from CHCl₃ (Found: C, 61.0; H, 6.15; S, 32.2. Calc. for C₁₅H₁₈S₃: C, 61.2; H, 6.12; S, 32.7%); i.r., Raman, and n.m.r. spectral data are given in Tables 1—3.

Reaction of endo-(6) *and* Na₂SO₃.—A solution of *endo*-(6) (0.80 g, 3.5 mmol) in acetone (25 cm³) was added to a solution of Na₂SO₃ (0.45 g, 3.5 mmol) in water (25 cm³).

A dense white precipitate formed and this was filtered off and thoroughly dried. This amorphous solid (0.72 g) had an analysis consistent with its formulation as the disulphide, $C_{10}H_{12}S_2$ (Found: C, 62.5; H, 6.26; S, 33.0. Calc. for

The solvent was stripped off to yield a yellow oil which was extracted with hot ethanol to remove triphenylphosphine sulphide (2.2 g, 7.4 mmol) which was identified by its m.p. 155 °C (lit., 156 °C) and i.r. spectrum. Further extraction

TABLE 1

The vibrational spectra (cm⁻¹) of the 1,2,3-trithiolans (below 2 000 cm⁻¹)

$C_7H_{10}S_3$		$endo$-$C_{10}H_{12}S_3$		exo-$C_{10}H_{12}S_3$		$C_{15}H_{18}S_3$		Assignments
I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r	Raman	
							110w	
	140w		128s				120s	
							155w	
			180m				165ms	
			203m				200m	
	226m				210m		215m	
	248w	278s	273s		278s	280m	280s	δ (S_3)
310vw	310m	312w	309s	315m	312m	315wbr	310m	δ (S_3)
							330m	
	354ms	352vw	349m		349ms		336s	δ (S_3)
			388w	415w	410w			
420w	420m	404w	413m			425mbr	422w	
				465s	459m			
490m	475m	420m	460m			470w	464w	ν_{as} (S_3)
	495m	485vs	485m	495s	490m	490s	482s	
		490vs					506s	
		518ms	514vs	515w	511vs		519vs	ν_s (S_3)
	545m			540s		530m	544m	
			596m	600w		550s		
						650w	653w	
678m	675ms	680vs	678m	670m	668m	680m	674s	ν_s (C–S)
	718w	695m	692m	705vsbr	705w	715s	713w	
	738ms	710vs	705m	730m		725w		
770s		745vs	740s	750s	750w	765w	776w	
806m	798vs	794vs	791w	795s	790w	790m	790w	
835w	820m	810m				810s	810w	
	850w		850w	835s	835mw	850m		
865wbr		878w				870w	882w	
875wbr	890w	890m				915m	911s	
885wbr								
		905m		910m				
925s	925w	920s	918w	920m	920m			
				935m	935vw		939w	
945sbr	955w	945vs	945vs	945w	945vw	940m	945w	
				955s		950m		
		970m		970m	970w	965s	963w	
		990m	990w			995s	996w	
1 002s	100w	1 005m	1 002w	1 010w	1 010w	1 010w	1 008w	
1 036w		1 035m	1 031w	1 035w	1 035w	1 030w	1 030w	
		1 050w	1 048w				1 051w	
		1 080m	1 080w	1 060m	1 065m	1 080m	1 068w	
		1 105m	1 102m	1 105w	1 110m	1 100w	1 098m	
							1 116m	
1 125w		1 128w				1 125m	1 125m	
1 142s		1 145m		1 140w		1 140m	1 132w	
		1 155m		1 155w	1 155w			
		1 164m		1 170w	1 170m			
1 180sbr		1 175m		1 189w				
		1 208m	1 205w	1 210wbr		1 210w	1 220m	
		1 220w	1 215w					
		1 240w		1 250w		1 235w	1 240m	
1 260s		1 260m		1 65m		1 260m		
1 268w		1 270m		1 275w		1 275s	1 278w	
		1 280m		1 290m		1 295w		
1 300vs		1 300m		1 300w			1 300vw	
		1 301m				1 315m		
1 315vs		1 325m		1 325m		1 325m		
		1 360m		1 355m		1 360m	1 360w	
			1 450w		1 450w		1 450w	
		1 610w	1 609m	1 620wbr	1 620w	1 610w	1 610m	ν_s (C=C)
			1 640wbr					

C_5H_6S: C, 61.2; H, 6.12; S, 32.7%); δ(SiMe₄) 1.5—3.2 (complex region, 10 H) and 5.7 (d, 2 H, CH olefinic).

Reaction of endo-(6) *and Triphenylphosphine.*—A solution of *endo*-(6) (2.28 g, 0.01 mol) in benzene (30 cm³) was mixed with a solution of triphenylphosphine (2.62 g, 0.01 mol) in benzene (30 cm³), and heated to reflux point for 15 min.

of the oil with $CHCl_3$ gave an amorphous solid identical to that obtained above, by desulphurization with Na_2SO_3, and with an analysis consistent with its formation as the disulphide, *i.e.* $C_{10}H_{12}S_2$ (Found C, 62.0; H, 6.21; S, 32.7%).

Heating of endo-(6).—A sample of *endo*-(6) (0.094 g, 0.4

mmol) was heated at 180 °C for 1 h. It slowly darkened from yellow through orange to brown with increasing temperature above its m.p. of 69 °C. At 180 °C the liquid became viscous. On cooling it gave a brittle solid soluble in CHCl3 from which it could be precipitated by methanol (the unpolymerized endo-C10H12S3 remains in solution) as an off-white solid, (C10H12S3)n (0.031 1 g, 0.14 mmol, 33.1%

addition of D2O to the sample, 3.25 (m, 2 H, CHSH); and 5.6 (m, 2 H, CH olefinic) with a complex region of signals at 1—2.5. The dithiol was converted into the lead dithiolate salt for a more thorough characterization. endo-C10H12-(SH)2 (0.31 g, 1.35 mmol) in ethanol (10 cm3) was mixed with a solution of Pb(CH3CO2)2·3H2O (23.6 g, 0.62 mol) in water and ethanol (50:50). An immediate yellow pre-

TABLE 2

^{1}H N.m.r. chemical shifts (p.p.m. SiMe4), description of spectra, and selected coupling constants (Hz) [see (9)]

Compound	H_a	H_b	H_c	H_d	H_e	H_f	Cyclopentene ring CH$_f$	CH=CH	
C7H10S3	1.05dm	1.94dm	3.64d	2.45m	1.21—1.73cr *				
endo-C10H12S3	1.30dm	2.10dm	3.70d	2.61dtr	3.26m		2.31dd	5.63dd	5.71dd
exo-C10H12S3	1.26dm	1.79dm	3.72d	2.23d		2.05—2.54cr	2.70m	5.50m	5.72m
C15H18S3	{ 1.05dm / 1.28d †	{ 1.94dm / 1.80d †	4.14d	2.74m / 2.22m †		2.10—2.60cr	3.05m	5.51m	5.62m

	J_{ab}	J_{ad}	J_{ac}
C7H10S3	8.0	1.5	2.1
endo-C10H12S3	10.3	1.5	2.1
exo-C10H12S3	10.7	1.5	0.9
C15H18S3	10.0	<1.0	1.5

* cr = complex region.   † Middle norbornane ring system.

conversion) (Found: C, 52.5; H, 5.3; S, 42.0. Calc. for C10H12S3: C, 52.6; H, 5.26; S, 42.1%). The i.r. and ^{1}H n.m.r. spectra of the polymer in CDCl3 were identical with those of the unpolymerized material. Another sample of endo-(6) heated for 1 h at 200 °C gave 97.2% conversion into the polymer.

Reaction of Norbornadiene and endo-(6).—Norbornadiene

TABLE 3

^{13}C n.m.r. chemical shifts/(p.p.m. from SiMe4) of 1,2,3-trithiolans

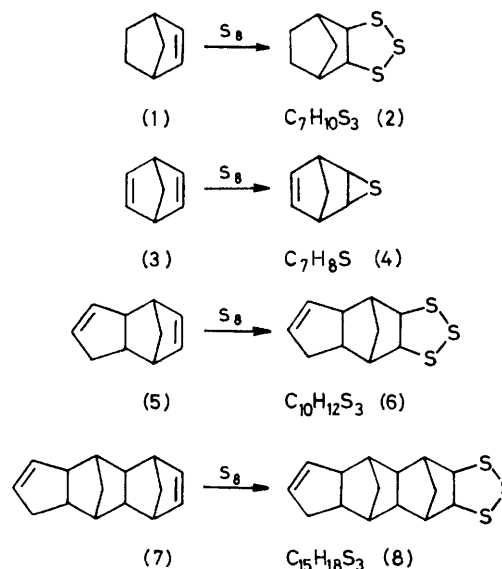| C7H10S3	exo-C10H12S3	endo-C10H12S3	C15H18S2	Assignment
	133.1	131.9	131.7	} olefinic C's
	130.4	130.6		
69.7	69.9	66.0	66.0	} trithiolan C's
	69.4	62.5	65.2	
	54.8	51.9	55.0	
	47.0			
	44.9	45.0	45.4	
			45.1	
44.0			44.0	
	42.9	43.6	43.6	
40.7		40.4	40.6	
			40.1	
	38.7		39.2	
		35.6	36.2	
32.3		31.6	31.7	} bridge C adjacent to trithiolan ring
	26.2			
28.7				} norbornane CH2's
27.6				

(1.1 g, 12 mmol) and endo-(6) (0.4 g, 1.75 mmol) were dissolved in CHCl3 (10 cm3) and left for 5 days. Removal of the volatile components left behind only unchanged endo-(6).

Reduction of endo-(6).—endo-(6) (3.0 g, 0.013 mol) in diethyl ether (20 cm3) was slowly added to a solution of sodium metal (2.3 g, 0.1 g atom) in liquid NH3 (100 cm3) at −78 °C. The mixture was allowed to warm to ambient temperature and an excess of NH4Cl was added to neutralize the solution. The product was extracted from the filtered ether solution, dried (MgSO4) by evaporation of the solvent to yield the dithiol, C10H12(SH)2 identified by its i.r. which showed ν(SH) at 2 525br cm^{-1} and ^{1}H n.m.r. spectra: δ(SiMe4) 1.75 (dd, 2 H, SH) these signals disappeared on

cipitate of *lead* endo-*cyclopentadiene dimer dithiolate*, endo-C10H12S2Pb, formed (0.14 g, 0.35 mmol, 23%), m.p. 180 °C (decomp.) (Found: C, 30.3; H, 3.2; S, 14.1%. Calc. for C10H12PbS2: C, 29.8; H, 3.00; S, 15.9%). The i.r. spectrum showed no ν(SH) but new peaks at 285s, 350m, 400m, 410m, and 465w cm^{-1}. The salt was insoluble in all solvents.

DISCUSSION

The reactions of elemental sulphur and the following olefins have been studied, norbornene (1),[4] norbornadiene (3), exo- and endo-cyclo-pentadiene dimer exo- and endo-(5), and cyclopentadiene trimer (7). In every case, with the exception of (3), the product contained a 1,2,3-trithiolan ring; the spectral data show that the trithiolan ring is exo in all four cases.

(1) $\xrightarrow{S_8}$ C7H10S3 (2)

(3) $\xrightarrow{S_8}$ C7H8S (4)

(5) $\xrightarrow{S_8}$ C10H12S3 (6)

(7) $\xrightarrow{S_8}$ C15H18S3 (8)

The product from (3) was the episulphide 7-thiatri-cyclo[4,3,0,1^{2,5}]oct-3-ene (*exo*-2,3-epithionorborn-5-ene),

C_7H_8S in 10% yield. The details of this compound are given at the end of the paper.

An attempt was made to prepare the trithiolan derivative of norbornadiene by sulphur exchange (1) in a manner analogous to that used to synthesize adducts of C_7H_8 and S_4N_4.[13] However the method was not successful and no exchange occurred.

$$C_7H_8 + endo\text{-}C_{10}H_{12}S_3 \longrightarrow C_7H_8S_3 + endo\text{-}C_{10}H_{12} \quad (1)$$
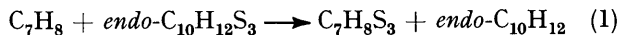
I.r. and Raman Spectra of the Trithiolans.—Table 1 lists the i.r. and Raman data for the four trithiolan derivatives. In cyclopentadiene dimer and trimer the stretching vibration of the norbornene double bond is at 1 570 cm^{-1} and this is absent in the trithiolans, whereas the band at ca. 1 610 cm^{-1} corresponding to the double bond of the cyclopentene remains.

The vibrational characteristics of C–S and S–S bonds are generally thought to be of little help in studying organic polysulphides.[14] However the vibrational spectra of the trithiolans are an exception to this truism and it has been possible to classify bands in the spectra clearly due to these bonds.

The stretching modes of the C–S bonds are generally weak in the i.r. region but they were readily identified in the range 675—720 cm^{-1} and, particularly, as a strong band at ca. 675 cm^{-1} in both the i.r. and Raman spectra.

The strongest band in all the Raman spectra is at 511—519 cm^{-1}, the corresponding band in the i.r. spectra being weak or absent. (It is this feature which makes S–S bonds difficult to identify on i.r. evidence alone.[15]) The band is thought to be a symmetric ring-stretching motion in which the S_3 atoms are chiefly involved. The stretching modes of H_2S_3 were assigned to Raman bands at 488 and 470 cm^{-1} (symmetrical and asymmetrical ν respectively),[16] with the latter having a strong i.r. counterpart at 471 cm^{-1}. The trithiolans have the corresponding asymmetrical stretching mode at 480—495 cm^{-1}, both i.r. and Raman active.

On the basis of its being common to the spectra of all the trithiolans a band at 309—312 cm^{-1} is assigned to a bending mode of the S_3 ring, as is strong Raman-active absorption at 273—280 cm^{-1}. The strong Raman line at 336—354 cm^{-1} may also be a ring deformation mode. These assignments are higher than those made for H_2S_3 but the nature of the cyclic trithiolan means that the bending modes will be most affected, and their energies increased.

To summarise the trithiolan spectra, it seems that m or s bands in the Raman picture at ca. 280, 310, 340, 480, and 515 cm^{-1} indicate the presence of such a ring system. The i.r. picture is of little help in confirming the structure.

^{1}H *and* ^{13}C *N.m.r. Spectra of the Trithiolans.*—Table 2 records the ^{1}H n.m.r. chemical-shift data for the trithiolans together with some relevant coupling constants for the bridge *anti*-proton. The characteristic features of the spectra produced by these trithiolans are those normally observed for norbornane compounds:[17] the AB quartet patterns of signals due to the bridge protons

H_a and H_b [see (9)] and the olefinic protons of the cyclopentene ring in *endo-* and *exo-*$C_{10}H_{12}S_3$ and in $C_{15}H_{18}S_3$.

(9)
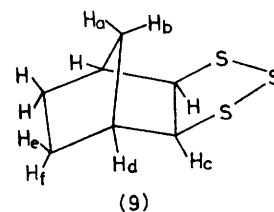
Most striking of all is the appearance of a sharp doublet (J 0.9—2.1 Hz) at δ 3.64—4.14 (SiMe$_4$). This arises from the protons attached to the carbon atoms of the trithiolan ring itself, *i.e.* H_c. The configuration of this ring system is thus confirmed as being *exo* in all cases. The *endo* protons H_c are coupled to the bridge *anti*-proton H_a. This was proved by the decoupling of the signal of H_c. In all the compounds the only change that resulted from this decoupling was a simplification of the signal of the H_a protons from a doublet of multiplets to a doublet (J_{ab} ca. 10 Hz) of triplets (J_{ad} ca. 1.5 Hz).

The ^{13}C n.m.r. spectra of the trithiolans are recorded in Table 3. The single signal for the carbon atoms in the trithiolan ring in $C_7H_{10}S_3$ is resolved into a pair by the asymmetry which comes with the introduction of the cyclopentene ring into the molecule. The effect of its presence on the carbon atoms of the trithiolan ring is at a maximum in *endo-*$C_{10}H_{12}S_3$, as is expected for a through-space effect, when Δδ is 3.5 p.p.m. (SiMe$_4$). For $C_{15}H_{18}S_3$ Δδ is 0.8 and for *exo-*$C_{10}H_{12}S_3$ is 0.5 p.p.m. (SiMe$_4$). Consequently the cyclopentene ring has the most effect on the bridge carbon in this last compound shifting the signal upfield by 5.4 p.p.m. compared to the signal of *endo-*$C_{10}H_{12}S_3$.

There are two anomalies in Table 3. The spectrum of $C_7H_{10}S_3$ should show only four signals of the four sets of non-equivalent carbon atoms. Six signals are observed—two at 27.6 and 28.7 p.p.m. for the CH$_2$ groups of the norbornane ring and two at 40.7 and 44.0 p.p.m. for the bridgehead groups. The secondly anomaly is the single signal for the non-equivalent olefinic carbon atoms in $C_{15}H_{18}S_3$.

endo-$C_{10}H_{12}S_3$.—This trithiolan is easy to prepare from readily available starting materials. It is a pale yellow crystalline solid with an indefinitely long shelf life. It is unaffected by boiling water, dilute acids, and dilute alkali. This stability is characteristic also of linear tertiary alkyl trisulphides such as $Bu^t_2S_3$.[18]

When heated, *endo-*$C_{10}H_{12}S_3$ melts at 69 °C to give a mobile yellow liquid, which darkens as the temperature increases, and polymerises above 170 °C—rapidly at 200 °C. This behaviour is reminiscent of elemental sulphur itself, except that the resultant polymer is a brittle solid at room temperature (compare plastic sulphur) which appears to be stable (compare the slow reversion of plastic sulphur to S_8).

endo-$C_{10}H_{12}S_3$ can be partly desulphurized by Na_2SO_3 and triphenylphosphine.[19] In each reaction an amor-

phous white solid was obtained that was soluble in $CHCl_3$, and analysed as $C_{10}H_{12}S_2$. It is thought to be a polymer.

$endo$-$C_{10}H_{12}S_3$ was reduced by Na–NH_3 [4] to give a smelly liquid thought to be the dithiol, $endo$-$C_{10}H_{12}$-$(SH)_2$, which was not fully characterized as such, but was converted into the stable, yellow lead salt, $endo$-$C_{10}H_{12}S_2Pb$. Reduction with $NaBH_4$ produced the expected H_2S [20] and a little of the dithiol but this reducing agent is not recommended.

C_7H_8S. No trithiolan formed in the reaction of norbornadiene and sulphur. Instead a yellow oil was obtained the analysis for which was consistent with its formulation as C_7H_8S and which we believe is the exo-episulphide (4). The i.r. spectrum (see Experimental section) shows the molecule to have a double bond still intact and also has the strong episulphide vibrational modes at 640 and 1 058 cm^{-1}.

The ^1H n.m.r. spectrum confirms the norbornene structure with the olefinic protons coupling with the bridgehead protons. The protons of the episulphide ring give a single signal at δ 3.92 ($SiMe_4$), no $anti,endo$ coupling as with the trithiolan protons. The bridge protons show a clear AB quartet.

Reported in the literature [21] is a compound, C_7H_8S, identified as $endo$-2,3-epithionorborn-5-ene which has signals at δ 5.73 (olefinic H), 3.25 (CHS), 3.02 (bridgehead H), and 2.08 (centre of 12 line pattern). The protons in this compound were labelled exo and the sulphide ring therefore $endo$. Consequently we feel confident in identifying our C_7H_8S compound as the exo-isomer, reported here for the first time.

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