

and ca. 66% *trans*-2-*tert*-butyl-5-carbomethoxy-1,3-dioxane, **14** and **15**, respectively. This isomeric mixture was separated by column chromatography (3% ethyl acetate/hexane) to give two oils as products: 16.8 g (30.6%) of the pure *trans* isomer, **15**, and 4.7 g (8.6%) of the pure *cis* isomer, **14** (yields are based on the starting dicarboxylic acid). For the *trans* isomer, **15**: $^1\text{H NMR}$ δ 0.9 (s, 9 H, C(CH₃)₃), 1.1-1.4 (t, J = 7 Hz, 3 H, CH₂CH₃), 1.6-1.7 (m, 1 H, CHCO₂), 3.4-4.5 (m, 7 H, CH₂-CH₃ and remaining ring H). For the *cis* isomer, **14**: $^1\text{H NMR}$ δ 0.9 (s, 9 H, C(CH₃)₃), 1.2-1.4 (t, J = 7 Hz, 3 H, CH₂CH₃), 2.1-2.3 (m, 1 H, CHCO₂), 3.5-4.6 (m, 7 H, CH₂CH₃ and remaining ring H). The *trans* isomer, **15** (6.8 g, 31.6 mmol), was dissolved in 100 mL of anhydrous ether, and this solution was added dropwise to a suspension of 3.0 g (79 mmol) of LiAlH₄ in 150 mL of anhydrous ether. After the suspension was stirred at room temperature for 2 h, it was carefully poured onto ice containing 0.3 g of solid NaOH, extracted with ether (2 × 75 mL), washed with brine, dried over Na₂SO₄, filtered, and evaporated to give 3.8 g (69%) of *trans*-2-*tert*-butyl-5-hydroxymethyl-1,3-dioxane, **16**, mp 59.0-60.5 °C: $^1\text{H NMR}$ δ 0.9 (s, 9 H, C(CH₃)₃), 1.9-2.6 (m, 1 H, CHCH₂OH), 3.2-4.3 (m, 7 H, CH₂OH and remaining ring H). To 1.0 g (5.7 mmol) of this compound dissolved in 16 mL of CH₂Cl₂ and cooled to -10 °C was added 1.5 g (5.7 mmol) of triphenylphosphine followed by 1.0 g (5.6 mmol) of *N*-bromosuccinimide. The mixture was stirred 10 min at -10 °C and then at room temperature for a further 30 min. Analysis by GC indicated the presence of *cis*- and *trans*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, **7 Br** and **8 Br**, respectively, in yields of 16.4% and 73.1%, respectively, together with unreacted starting material (3.6%) and the isomerized, i.e., *cis*, starting alcohol (6.9%). Evaporation of the

reaction mixture, treatment with 50 mL of 5% ethyl acetate/hexane, filtration, and column chromatography (5% ethyl acetate/hexane) gave 0.8 g of a mixture consisting of ca. 20% of the *cis*, **7 Br** and ca. 80% of the *trans*, **8 Br**, bromomethyl compounds. Preparative GC gave the pure (>95%) isomers. *Cis*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, **7 Br**, mp 35.2-36.1 °C: $^1\text{H NMR}$ (400 MHz) δ 0.89 (s, 9 H, C(CH₃)₃), 1.70-1.74 (br t, J = 7.3 Hz, 1 H, CHCH₂Br), 3.72-3.74 (d, J = 7.3 Hz, 2 H, CH₂Br), 3.89-3.91 (d, J = 11.2 Hz, 2 H, (H_{ax}CH_{eq})₂), 4.10 (s, 1 H, CHC(CH₃)₃), 4.13-4.16 (d, J = 11.2 Hz, 2 H, (H_{ax}CH_{eq})₂); $^{13}\text{C NMR}$ δ 24.50, 30.00, 33.64, 37.83, 68.39; GC/MS, m/e (rel intensity) 237 (M - 1 ⁸¹Br, 1.8), 235 (M - 1 ⁷⁹Br, 2.06), 181 (96.0), 179 (100), 135 (12.5), 133 (12.2). *Trans*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, **8 Br**, mp 27.7-28.4 °C: $^1\text{H NMR}$ (400 MHz) δ 0.90 (s, 9 H, C(CH₃)₃), 2.26-2.31 (m, 1 H, CHCH₂Br), 3.09-3.11 (d, J = 6.2 Hz, 2 H, CH₂Br), 3.38-3.44 (t, J = 11.5 Hz, 2 H, (H_{ax}CH_{eq})₂), 4.00 (s, 1 H, CHC(CH₃)₃), 4.18-4.22 (dd, J = 11.5 Hz and 4.4 Hz, 2 H, (H_{ax}CH_{eq})₂). $^{13}\text{C NMR}$, δ 24.76, 29.63, 34.74, 36.10, 70.71; GC/MS, m/e (rel intensity) 237 (M - 1 ⁸¹Br, 2.15), 235 (M - 1 ⁷⁹Br, 2.22), 181 (93.9), 179 (100), 135 (10.5), 133 (13.0).

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Supplementary Material Available: Figure 4 showing one main line of the EPR spectrum of **1a** and **2a** (1 page). Ordering information is given on any current masthead page.

Chemical Reactivity of the Three-Sulfur Ring in Norbornanetrithiolanes. The S₃ Transfer Reaction

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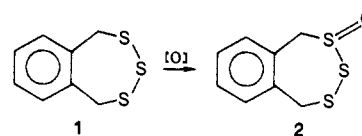
Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. Received March 7, 1988

Abstract: The oxidation of norbornanetrithiolanes with *m*-chloroperbenzoic acid and with ozone has been studied in detail. The trithiolane 1- and 2-oxides are formed, their ratio depending on the substitution at C₂ of the norbornane framework. In some cases it has been possible to separate the *exo* and *endo* isomers of these oxides. Heating *endo*-2-phenyl-*exo*-3,4,5-trithiatriacyclo[5.2.1.0^{2,6}]decane (**8**) with norbornene at 100 °C gives *exo*-3,4,5-trithiatriacyclo[5.2.1.0^{2,6}]decane (**3**) and 2-phenylnorbornene. Thus, for the first time an S₃-transfer reaction has been observed. A thorough kinetic analysis of this reaction has been carried out, and the results indicate a bimolecular concerted mechanism.

In a recent study¹ we have shown that a variety of norbornene double bonds react with elemental sulfur to give norbornanetrithiolanes and -pentathiepanes. Here we report on (i) oxidation of norbornanetrithiolanes with different oxidizing reagents and (ii) the capability of some of the trithiolanes to act as donors of the "S₃" unit.

Introduction

Oxidation of monosulfides to sulfoxides and sulfones is an actively researched branch of organosulfur chemistry. In recent years the oxidation of disulfides has also received considerable interest.^{2,3} Feher et al.⁴ have shown that oxidation of linear trisulfides with excess of peroxides gives symmetrical disulfonyl sulfides, suggesting that the middle sulfur is least prone to attack. This observation has also been found to be true in the oxidation of the benzotrithiepane (**1**).⁵



We have carried out a systematic study of the oxidation of norbornanetrithiolanes by different oxidizing agents. This study has revealed that the norbornane framework exerts some unique control on the regio- and stereochemistry of oxidation.

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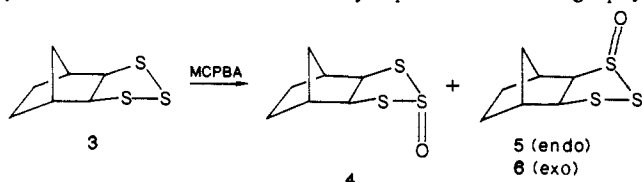
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Table I. Significant ^{13}C and ^1H NMR Chemical Shifts of **3**, **8**, and Their Corresponding Trithiolane *n*-Oxides

no.		C_2	C_6	H_2	H_6	H_{10s}	H_{10a}
3		69.70	69.70	3.60	3.60	1.82	1.05
4		71.32	71.32	4.70	4.70	1.95	1.21
7		79.70	79.70	4.80	4.80	2.50	1.38
6		87.36	59.94	3.75	3.39	1.95	1.25
5		87.10	70.97	3.95	3.25	2.03	1.25
8		86.90	69.30		4.00	2.48	1.30
9		75.14	86.70		3.70	2.45	1.55
10		87.10	87.91		3.30	2.40	1.50
16		100.75	80.29		4.65	2.90	1.63
17		94.71	75.98		5.08	2.40	1.50

Results and Discussion

Oxidation with *m*-Chloroperbenzoic Acid (MCPBA). When **3** was treated with 1 equiv of MCPBA, three oxides in an overall yield of 50% could be isolated. By repetitive chromatography



the major component, *exo*-3,4,5-trithia-*endo*-4-oxotricyclo-[5.2.1.0^{2,6}]decane (**4**), could be separated from the mixture while the unsymmetrical trithiolane 1-oxides (**5** and **6**) were inseparable. A reviewer has suggested that the IUPAC nomenclature for one compound for each class of these heterocyclic compounds should appear once in the text. To make the paper more readable, we will use the term *trithiolane* for the unoxidized and *trithiolane n-oxide* for the oxidized species, where *n* indicates the oxidized sulfur atom in a 1,2,3-trithiolane. The symmetrical nature of **4** was evident from its four-line ^{13}C NMR spectrum (Table I), and that it was the central sulfur that had been oxidized was evident from the similarity in the chemical shifts of C_2 and C_6 compared to those for **3**. Similarly, the unsymmetrical nature of **5** and **6** was supported by a 14-line ^{13}C NMR spectrum of the mixture. Although it is tempting to assign the *endo* stereochemistry for **4** on the basis of NMR evidence alone (i.e. downfield shift of 1.00 ppm for the H_2 and H_6 protons), the evidence is insufficient since the *exo* isomer **7** (vide infra) shows a similar shift. In fact it was an X-ray analysis²⁵ that confirmed the *endo* structure (Figure 1).

Although all efforts to separate **5** and **6** failed, one way of establishing that they represent a case of *exo* and *endo* isomerism

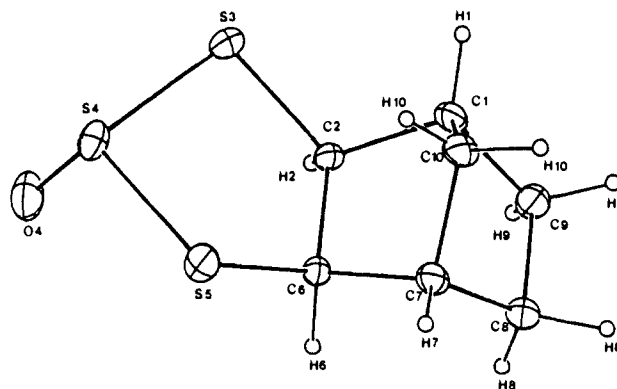


Figure 1. ORTEP diagram of **4**.

would be to oxidize them further to a single dioxide. Oxidation of a sulfoxide to a sulfone in the presence of a sulfide has been accomplished by using KMnO_4 as the oxidizing agent.^{7,8} When an aqueous solution of KMnO_4 was added to a mixture of **5** and **6**, there was immediate decolorization. Workup gave an oil exhibiting NMR (^1H and ^{13}C) spectra identical with that of one of the initial monooxides. Thus, it seems that KMnO_4 destroys the more reactive isomer (thermal instability of trithiane sulfones has precedence⁹).

(7) Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 5715.

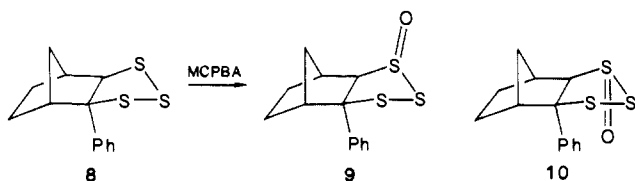
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(9) Johnson, C. R.; Drefenbach, H.; Keiser, J. E.; Sharp, J. C. *Tetrahedron* **1969**, *25*, 5649.

Table II. ^1H and ^{13}C NMR and IR Data for 4 and 7

		NMR, δ	
C_1, C_7	42.40 (d)	45.43 (d)	
C_2, C_6	71.32 (d)	79.70 (d)	
C_8, C_9	27.05 (t)	27.53 (t)	
C_{10}	32.19 (t)	32.57 (t)	
H_2, H_6	4.70 (d, $J = 2$ Hz)	4.80 (d, $J = 2$ Hz)	
H_1, H_7	2.53 (m)	2.60 (m)	
H_{10s}	1.95 (d, $J = 10.6$ Hz)	2.50 (d, $J = 10.6$ Hz)	
H_{10a}	1.28 (dt, $J_1 = 10.6$ Hz, $J_2 = 2$ Hz)	1.38	
$\text{H}_{8n}, \text{H}_{9n}$	1.68–1.83 (m)	1.70 (m)	
$\text{H}_{8x}, \text{H}_{9x}$	1.32–1.44 (m)	1.38 (m)	
		IR, cm^{-1}	
$\text{S}=\text{O}$	1100	1090	

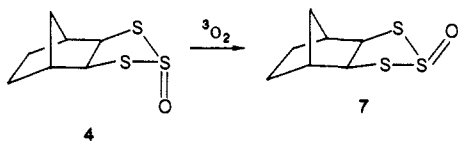
MCPBA oxidation of **8** at 0°C gave two products analyzed by NMR and TLC. The ratio of the products as determined by ^1H NMR was 2:1, and they could be separated by chromatography. Assuming steric hindrance for approach of reagent from the endo face of **8** due to the presence of the phenyl group, the major trithiolane 2-oxide **9** has been assigned the exo configuration.



That exclusive terminal sulfur oxidation had taken place was clearly evident from the 19 ppm downfield shift of C_6 in both **9** and **10** with respect to **8** (Table I). That no middle sulfur oxidation had occurred was evident from the absence of significant downfield shift of H_6 in either **9** or **10**. Although the two isomers do not show major differences in their ^1H NMR spectrum, there is a significant difference in the absorption of the carbon bearing the oxidized sulfur atom. In **9** this carbon (C_2) absorbs about 10 ppm upfield from that of the endo isomer **10** (which has a chemical shift very similar to the parent trithiolane). Although we have no explanation for this difference, a similar difference in absorption was observed in the pair **5** and **6**.

One significant difference in the MCPBA oxidations of **3** and **8** is the complete lack of oxidation of the middle sulfur in **8**.

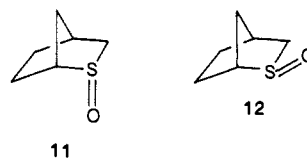
Isomerization of a Trithiolane 2-Oxide. A very interesting observation in this series of trithiolane oxides is the O_2 -catalyzed isomerization of **4**. An NMR sample of pure **4** sitting on the



bench top for 6 months was found to consist of a 1.2:1 mixture of **4** and **7**. The mixture on mass spectral analysis gave an M^+ with m/e 206, suggesting a mixture of monooxides rather than a monooxide-dioxide mixture. The two isomers could be separated by chromatography. The endo assignment of **4** has already been proven by crystal structure. The exo nature of **7** could be easily assigned by comparing ^1H NMR and IR data with those of **4** (Table II).

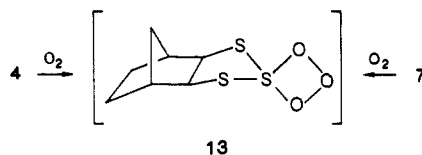
A four-line ^{13}C NMR spectrum for **7** indicated it to be a symmetrical trithiolane oxide. For **7** where the oxygen is exo, the syn H_{10} proton absorbs at δ 2.50 while in the endo isomer **4** the deshielding due to the oxygen is absent and hence the syn H_{10} proton resonates at δ 1.95, close to δ 1.82 in the parent trithiolane

3. The endo- and exo-sulfoxides **11** and **12** are reported⁹ to show considerable similarity in their IR and UV data whereas the NMR spectra are quite dissimilar (not reported).



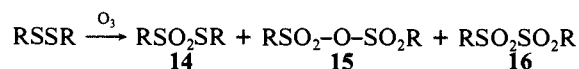
Stirring pure **4** under argon for 7 days did not result in any conversion to **7**. On the other hand, when the argon atmosphere was replaced by O_2 , the equilibrium was achieved in 4 days. Thus, O_2 is necessary for the isomerization to take place. Simple sulfoxides are reported to be sterically much more stable than other isoelectronic compounds such as amines, phosphines, or carbanions and do not undergo thermal isomerization easily except for benzylic and allylic sulfoxides.¹⁰ To the best of our knowledge, the isomerization of **4** by O_2 is the first of its kind.

The simplest mechanism that may explain the order of events is direct attack of $^3\text{O}_2$ on the sulfoxide sulfur to give the symmetrical trioxide **13**, which could then decompose by scission of either S–O bond to give **4**, **7**, and O_2 . The intermediate **13** can also be viewed as the primary intermediate between O_3 and **3**. To determine whether such a mechanism was operative, the study of the reaction between O_3 and trithiolane was undertaken.



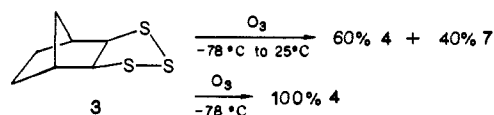
Ozonation of Trithiolanes. Although a large number of ozonation studies have been carried out on thioethers and open-chain di- and tetrasulfides,^{11–13} we are not aware of any studies on the ozonation of cyclic polysulfides.

In the ozonation of open-chain disulfides^{14,15} (which were found to be 40–50 times less reactive than thioethers) the corresponding thiosulfonates **14** and sulfonic anhydrides **15** could be isolated, their yields depending upon the reaction conditions, together with traces of disulfide **16**.



Ozonation of tetrasulfides¹⁶ gave the corresponding sulfonic anhydride and SO_2 as the only product.

When a solution of **3** in CH_2Cl_2 was saturated with O_3 at -78°C and allowed to attain room temperature, two products **4** and **7** in a 3:2 ratio could be isolated in an overall yield of 60%. The



major product **4** had NMR and IR spectra identical with those of the symmetrical trithiolane oxide obtained in the MCPBA oxidation of **3**, whereas the minor product **7** exhibited spectral data that were superimposable on those obtained for the trithiolane oxide formed from **4** on exposure to O_2 . When the ozonation was

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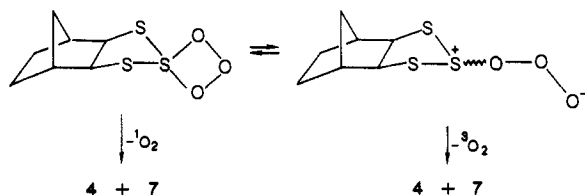
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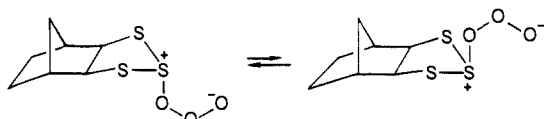
(16) Field, L. C.; Laceyfield, W. B. *J. Org. Chem.* **1966**, 31, 3555.

carried out at $-78\text{ }^{\circ}\text{C}$ with the excess O_3 and O_2 being removed by a stream of N_2 , **4** was obtained as the only product. Although **4** has been found to react with O_2 to give **7**, the reaction is very slow (7 days for 50% conversion); hence, the formation of **7** from **4** due to the presence of O_2 in O_3 can be ruled out. Also when **4** was exposed to O_3 at $0\text{ }^{\circ}\text{C}$, no significant transformation could be detected. Thus, the ozonation experiments seem to support the initial idea that the oxygen-catalyzed isomerization of **4** probably involves an intermediate like **13** that is also generated in the direct ozonation of **3**.

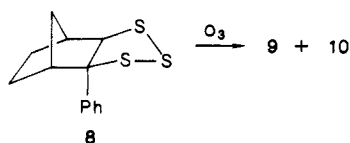
One other aspect of the isomerization and ozonation reaction is the possibility of $^1\text{O}_2$ generation during the thermal breakdown of **13**. This is a possibility if the trioxide is cyclic and the breakdown is concerted. On the other hand **13** could very well



be in equilibrium with the open-chain trioxide which would release $^3\text{O}_2$ to give the oxide. If $^1\text{O}_2$ is being generated, it should be possible to trap it with adamantylideneadamantane (Ad=Ad), which is known to react with $^1\text{O}_2$ to give a stable, easily detectable dioxetane.¹⁷ A solution of **3** was saturated with O_3 at $-78\text{ }^{\circ}\text{C}$, the excess O_3 was removed by bubbling N_2 , and Ad=Ad was added. The solution was then allowed to warm to room temperature. Analysis of the reaction mixture revealed complete conversion of **3** to **4** while the Ad=Ad remained unreacted. Neither NMR nor vpc analysis indicated the formation of dioxetane. Inability to trap $^1\text{O}_2$ suggests that the intermediate trioxide is present primarily in the open-chain form. This conclusion is based on the assumption that **13** is stable at $-78\text{ }^{\circ}\text{C}$ and decomposes to **4** only when warmed. The formation of only **4** at $-78\text{ }^{\circ}\text{C}$ indicates that the *endo*-trioxide is kinetically favored and equilibrates to a mixture of *endo* and *exo* at higher temperatures, giving a mixture of sulfoxides at room temperature. This again reflects that the favored approach of reagents to **3** is from the *endo* face of the sulfur ring. This also explains the formation of only **4** in the MCPBA reaction, here the bulky MCPBA showing greater stereoselectivity than O_3 or O_2 .



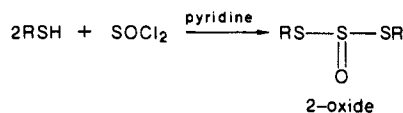
Ozonation of **8** at $-78\text{ }^{\circ}\text{C}$ gave **9** and **10** with NMR spectra identical with those obtained in the MCPBA oxidation. The relative amounts of **9** and **10** were also found to be similar. In



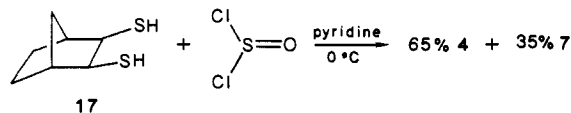
contrast to **3**, no oxidation of the middle sulfur was observed. Since neither MCPBA nor O_3 was able to oxidize the middle sulfur of **8**, it was decided to attempt an independent synthesis of trithiolane 2-oxides. This would enable us to establish a correlation between NMR chemical shifts and oxidation state of a particular sulfur atom for the oxides of **8** as has been obtained for the trithiolane 1- and 2-oxides of **3**.

Independent Synthesis of Trithiolane 2-Oxides. The formation of **4** in the MCPBA oxidation of **3** can be regarded as rather unique since all oxidations of acyclic trisulfides (regardless of the alkyl groups) invariably give the 1-oxides. The 2-oxides on the

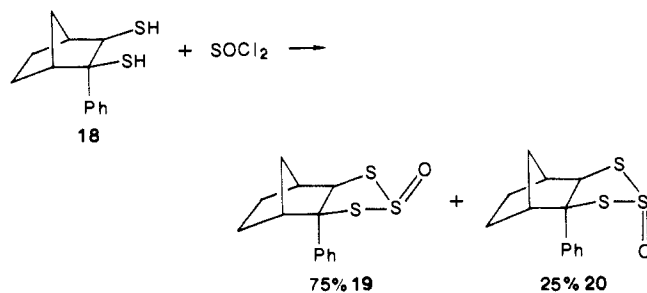
other hand have to be independently synthesized by the reaction of 2 equiv of the individual alkanethiols with thionyl chloride (SOCl_2) in the presence of pyridine.¹⁶ Thus, to be absolutely sure that **4** was being formed in the MCPBA reaction (and also during ozonation), we decided to synthesize the 2-oxides by this method.



The reaction between equimolar amounts of dithiol **17**¹⁸ and SOCl_2 in the presence of pyridine at $0\text{ }^{\circ}\text{C}$ gave a 44% yield of the 2-oxides **4** and **7** with **4** being the major component, a result very similar to that obtained in the ozonation of **3** at $0\text{ }^{\circ}\text{C}$.



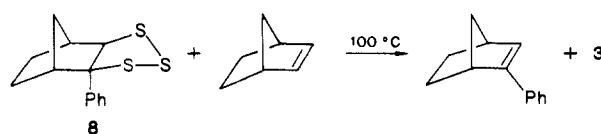
Dithiol **18** could be easily synthesized in high yield by LiAlH_4 reduction of **8**. When **18** and SOCl_2 were stirred in the presence of pyridine, two isomeric 2-oxides could be isolated in 64% yield. When the chemical shift of the *syn* H_{10} proton was compared, the sulfoxide with the most downfield shift for this proton was assigned as the *exo* isomer **19** and the other the *endo* 2-oxide **20** (Table I). The observation that the chemical shift of H_6 is influenced by the oxidation state of the middle sulfur seems to be valid in this case also. In both **19** and **20** H_6 absorbs about 1.0 ppm downfield in comparison to H_6 in the parent trithiolane **8**.



An interesting aspect of the result of this reaction is the complete reversal of stereoselectivity. Whereas the *endo*-2-oxide is the only or major product for the unsubstituted trithiolane **3**, it is the *exo*-2-oxide that is the major product when an *endo* phenyl group is introduced. Such a through-space steric effect of a phenyl substitution at the α -carbon bearing the S_3 unit on the middle sulfur of the trithiolane ring is in harmony with the deshielding effect the middle sulfur has on the group α to the carbon bearing the S_3 unit.

S_3 -Transfer Reaction. The observation that **8** decomposed smoothly to the olefin under gas chromatographic condition ($100\text{ }^{\circ}\text{C}$)¹ suggested that it had the potential for acting as a source of the interesting S_3 unit.

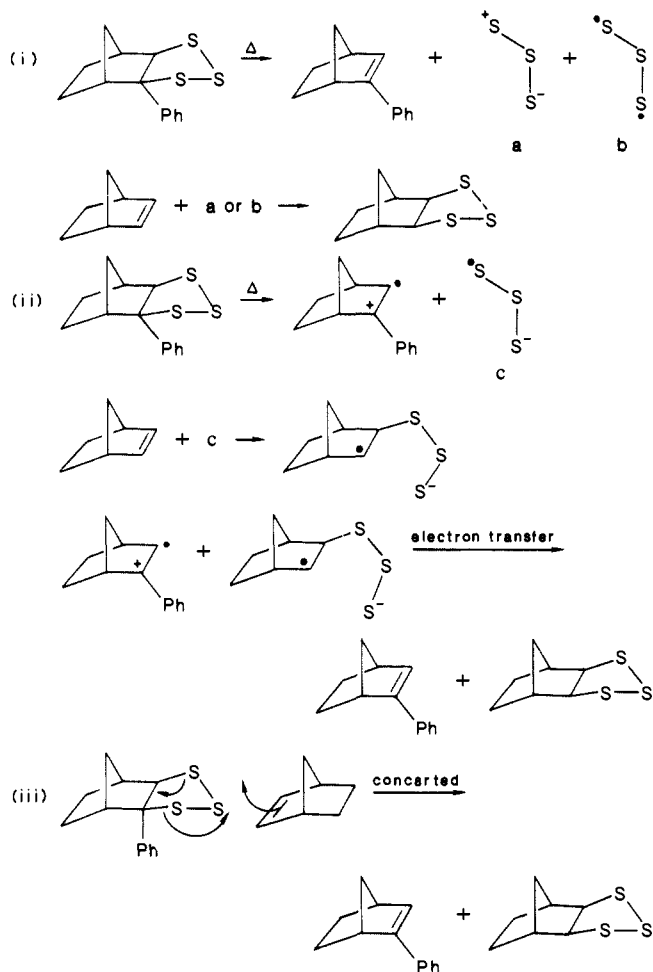
Heating equal amounts of **8** and norbornene in benzene at $100\text{ }^{\circ}\text{C}$ resulted in a clean S_3 transfer, giving 2-phenyl-2-norbornene and the well-characterized norbornanetrithiolane (**3**) quantitatively. This reaction could also be regarded as a phenyl group



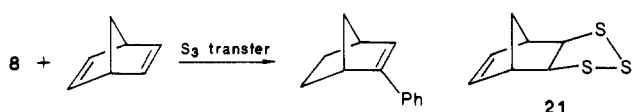
transfer reaction. That this was not the case was easily proved by performing the reaction with norbornadiene as the acceptor. Heating norbornadiene and **8** gave **21** as the only isolable trithiolane. If phenyl transfer were operating, then the products should have been 2-phenylnorbornadiene (which could have been

(17) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169.

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

Scheme I. Various Pathways for S₃ Transfer

easily detected as an authentic sample of the diene was available) and **3**, none of which was detected.



Three different pathways can be visualized for the S₃-transfer reaction (Scheme I). The first involves a thermal cleavage of **8** homolytically or heterolytically to give phenyl-norbornene and a dipolar or diradical S₃, followed by addition to norbornene. The second pathway, which is similar to the first, involves radical ions instead of neutral or radical molecules. A driving force for this type of cleavage would be the location of the positive charge on the phenyl-substituted carbon. In the last step of this pathway, the two new radical ions take part in an electron-transfer process to give the products. The third possibility is a bimolecular concerted¹⁹ transfer of the S₃ unit.

In a control experiment **8** did not undergo any decomposition when heated near 100 °C for extended periods of time, indicating the probable absence of the dissociation of an S₃ unit in the first step, which should result in the deposition of sulfur. Heating **8** and norbornene in the presence of the free-radical inhibitor 2,4-di-*tert*-butyl-*p*-cresol gave a smooth S₃ transfer. No inhibition was observed, thus ruling out a free-radical-mediated S₃ transfer, involving a high chain length in which a very sensitive radical is a key link. A second-order kinetic analysis of the reaction was

(19) The term "concerted" is used here, as in most discussions of reaction mechanisms to denote a process in which no energy minimum intervenes between reactants and products. There is no implication concerning symmetry of the transition state or synchronism of changes in different parts of the reaction complex.²⁰

(20) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

Table III. Rates of S₃ Transfer in Different Solvents Using Different Donors

no. (R)	concn, M	norbornene, M	solvent	temp, °C	$k_2 \times 10^2, M^{-1} \text{ min}^{-1}$
8 (H)	0.32	0.32	C ₆ D ₆	102.2	2.02
8 (H)	0.32	0.32	C ₆ D ₅ NO ₂	102.2	2.06
22 (OCH ₃)	0.32	0.32	C ₆ D ₆	101.8	7.14

Table IV. Dependence of Rate on Temperature for S₃ Transfer between **8** and Norbornene

temp, °C	$k_2 \times 10^2, M^{-1} \text{ min}^{-1}$	$E_a, \text{ kcal/mol}$	$\Delta S^\ddagger, \text{ eu}$
85.0	0.30		
101.6	1.90	27.8	-2.9
126.8	20.00		

carried out using different donor molecules in solvents of different polarity.

The results of these studies are shown in Table III. These kinetic results clearly show that solvent polarity has no effect on the overall rate of this reaction, since the rate of transfer of S₃ from **8** is identical in benzene ($\epsilon = 2.5$) and nitrobenzene ($\epsilon = 35$). This rules out the possibility for involvement of polar intermediates. On the other hand *p*-anisyl-norbornanetrithiolane (**22**) transfers S₃ 3.5 times faster than the parent system **8**. In the hydrolysis of norbornyl chlorides it is known²¹ that substituting a *p*-anisyl group at the 2-position increases the rate by a factor of 1000 compared to the rate obtained for 2-phenyl-2-norbornyl chloride. In the case of hydrolysis, which involves discrete ionic intermediates, there is a significant rate enhancement, while in the S₃-transfer reaction a rate enhancement of 3.5 is comparatively insignificant to indicate an ionic pathway. On the other hand, unequal bond formation and bond breaking in the transition state of the concerted pathway would probably explain the slight increase in rate.

To get an idea of the thermochemistry involved in the reaction, the dependence of rate of transfer on temperature was investigated. Rates were measured at 85.0, 101.6, and 126.8 °C. The rates and the values for E_a and ΔS^\ddagger are shown in Table IV. Since the number of components reacting is equal to the number of product species, there is no loss or gain in the overall degrees of freedom and hence a ΔS^\ddagger of zero should have been expected. A value of -2.9 eu is in agreement with an ordered transition state during the transfer process.

Although there are no reports on the existence of such an S₃-transfer reaction,²² the transfer of hydrogen from diimide to an olefin²³ is probably the best example with which one can compare this reaction. Thus, like the diimide reaction the S₃-transfer reaction can be viewed as a case of double-group transfer.²⁴

When **8** and 2-methyl-2-norbornene were heated for 6 h, only 7% transfer was observed to give trithiolane **23**. Continuing the

(21) Brown, H. C. *The Nonclassical Ion Problem*; Plenum: New York, 1977; p 153.

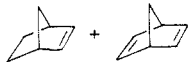





(22) Recently there have been two reports on the existence of an "S₂" transfer: (a) Schmidt, M.; Gori, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 887. (b) Steliou, K.; Salama, P.; Drodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926.

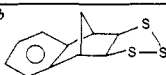
(23) Hunig, S.; Muller, H. R.; Thier, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271.

(24) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: GmbH, 1970; p 141.

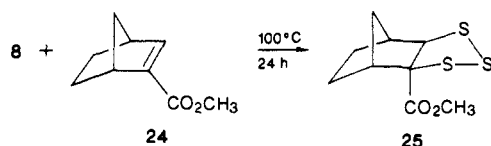
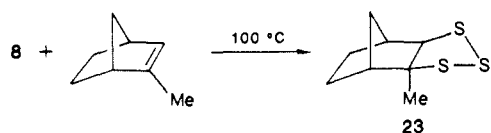
(25) Watson, W. H., private communication. We thank Prof. Watson for the information on which Figure 1 is based.

Table V. Competitive Trithiane Transfer

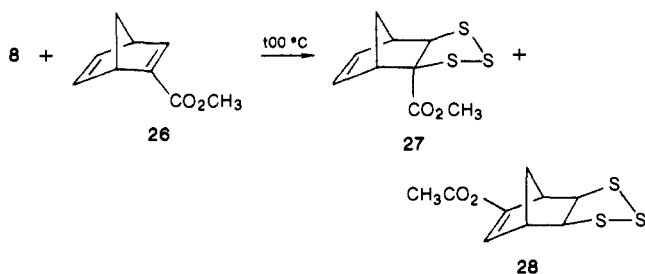
donor	acceptors	time, h	trithiolane (yield, ^a %)
8	 + 	6	3 (57) + 21 (43)
8	 + 	6.5	3 (69) + 29 ^b (31)
8	 + 	7	3 (100) + 23 (0)

^aRelative yields were determined by ¹H NMR. ^b

heating for 24 h gave 30% transfer. It should be noted that under identical conditions **8** gives 90% transfer with norbornene.



Heating 2-carbomethoxy-2-norbornene (**24**) with **8** for 24 h gave a 68% isolated yield of trithiolane **25**. Diene **26** when heated with **8** for 12 h gave a 40% yield of the two trithiolanes **27** and **28**, both being formed in equal amounts.



The only trithiolanes that have so far been observed to act as potential donors of the S₃ unit are **8** and **22**. Since none of the unsubstituted norbornanetrithiolanes exhibited donor properties, the substitution seems to play a very important role. The enhanced reactivity of **8** and **22** could be attributed to local steric and/or electronic effects introduced by the phenyl group. In trying to distinguish between these effects, both **23** and **25** were subjected to the transfer reaction as donor molecules.

Heating a solution of **23** and norbornene in benzene at 102.0 °C for 12 h failed to show any S₃ transfer. Removal of benzene and norbornene gave back **23**. When **25** was heated with norbornene for 12 h, only 14% transfer was observed. Thus, neither **23** nor **25** demonstrated a donor ability comparable to that of **8** or **22**, indicating that the electronic contribution of the aryl group is more important than its steric bulk for the release of S₃.

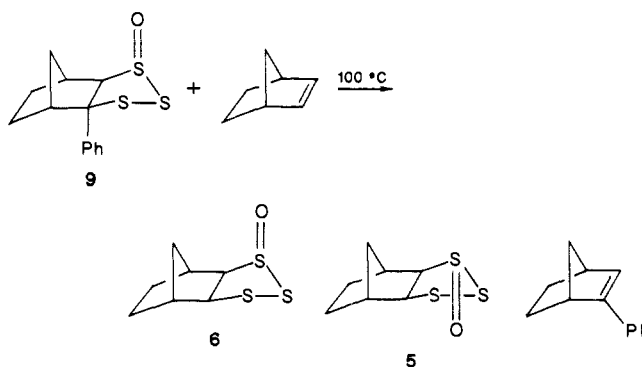
In order to get some insight as to which molecule would serve as the best acceptor of an S₃ unit, a few competitive experiments were carried out. In these experiments one acceptor was norbornene while the other acceptor was varied. One equivalent of **8** was used as the donor.

The results indicate (Table V) that norbornadiene and benzonorbornadiene are similar in reactivity whereas parent norbornene is the best acceptor of all. A methyl substituent drastically reduces accepting ability, indicating that unsubstituted norbornene bonds are best suited to act as acceptors.

Transfer of the -S(O)SS- Fragment. The ability of **8** to transfer an S₃ fragment suggested that **9** and **10** might possess the ability

to transfer the -S(O)SS- fragment. If such a transfer is feasible, it would be desirable to know whether the stereochemistry of the oxygen in the donor molecule would be retained in the acceptor molecule.

When a solution of pure **9** and norbornene in benzene was heated at 100 °C for 12 h, 50% yield of the two norbornane trithiolane 1-oxides **5** and **6** was obtained, together with 2-phenylnorbornene and some polymeric material that could not be characterized. From the ¹H NMR spectrum the ratio of **5**:**6**



was found to be 2.7. Although this result by itself indicates complete loss of stereochemistry of the oxygen during the transfer process, an identical reaction with the endo isomer **10** gave the same ratio of **5** and **6**. On the other hand, when a mixture of **5** and **6** (**6**:**5** = 1.7) was heated at 100 °C for 12 h, ¹H NMR analysis revealed the composition to be **5**:**6** = 2.7. When **9** was heated for extended periods of time, extensive decomposition was observed and the remaining trithiolane oxide was still found to be **9**. Although no endo-oxide **10** could be detected, neither could the decomposition products be characterized.

Thus, from these preliminary studies no conclusion can be drawn regarding the stereospecificity of the -S(O)SS- transfer reaction. However, the reaction in itself can be explored to synthesize trithiolane 1-oxides for further studies.

Conclusion

This initial study indicates that simple norbornanetrithiolanes can serve as good models for the study of trisulfide oxidation. Due to the presence of the norbornane framework, products are readily identified by NMR spectroscopy. Although some relationships between the position and reactivity of a particular sulfur atom have been observed, more research is required to make any definite claims on the factor(s) governing these relationships.

A significant outcome of this present study has been the S₃-transfer reaction. The potential of this reaction as a synthetic and mechanistic tool remains to be determined.

Experimental Section

General Procedures. Infrared (IR) spectra were recorded on a Perkin-Elmer 1907 spectrophotometer. ¹H NMR spectra were obtained on a Varian EM-390, 90-MHz spectrometer and a Varian XL-300, 300-MHz spectrometer with Me₄Si as internal reference unless otherwise noted. ¹³C NMR spectra were obtained on a Jeol FX-60 and Varian XL-300 spectrometer operating at 15 and 75 MHz, respectively. All spectra were obtained in CDCl₃ 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. Ozonolyses were performed on a Welsbach ozonator, Model T-23, producing 4% ozone in oxygen. The silica gel used for column chromatography was 60–200 mesh obtained from Baker Chemical Co. Preparative TLC was performed on 20 × 20 cm glass plates coated with silica gel (1000 μm) obtained from Analtech Inc. Elemental analyses 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.

Trithiolanes **3** and **8** were prepared by known methods.¹

General Procedure for MCPBA Oxidation. To a solution of the trithiolane (0.5–2.0 mmol) in 15 mL of methylene chloride (CH₂Cl₂) at 0 °C was slowly added 1 equiv of 80% MCPBA in CH₂Cl₂. After the addition the solution was stirred for 1 h. The precipitated *m*-chlorobenzoic acid was filtered off and the filtrate washed with 10% sodium bisulfite followed by 10% sodium bicarbonate solution and finally brine. The CH₂Cl₂ layer was then dried over sodium sulfate and the solvent removed under reduced pressure. The products were isolated by chromatography.

Oxidation of 3. A solution of **3** (380 mg, 2 mmol) was treated with 450 mg of 80% MCPBA. The crude product was chromatographed over silica gel with pentane–ethyl acetate (4:1) as eluent to give 120 mg (29%) of **4** (*R_f* 0.5) and 100 mg (24%) of **5** and **6** as an inseparable mixture (*R_f* 0.4). For **4**: mp 42–44 °C; ¹H NMR δ 4.70 (d, *J* = 2 Hz, 2 H), 2.53 (d, 2 H), 1.95 (d, *J* = 10.6 Hz, 1 H), 1.68–1.83 (m, 2 H), 1.32–1.44 (m, 2 H), 1.21 (dt, *J*₁ = 10.6 Hz, *J*₂ = 2 Hz, 1 H); ¹³C NMR 71.32 (d), 42.40 (d), 32.19 (d), 27.05 (t) ppm; IR 2950, 1440, 1300, 1290, 1100 (s), 995 cm⁻¹; mass spectrum for C₇H₁₀OS₃, calcd 205.9895, obsd 205.9894. For **6**: ¹H NMR δ 3.75 (dd, *J*₁ = 7 Hz, *J*₂ = 2 Hz, 1 H), 3.39 (dd, *J*₁ = 7 Hz, *J*₂ = 2 Hz, 1 H), 2.87 (m, 1 H), 2.40 (m, 1 H), 1.95 (dt, *J*₁ = 10 Hz, *J*₂ = 2 Hz, 1 H), 1.62–1.86 (m, 2 H), 1.16–1.35 (m, 3 H); ¹³C NMR 87.36, 59.94, 42.00, 38.94, 34.62, 27.99, 27.78 ppm. For **5**: ¹H NMR δ 3.95 (dd, *J*₁ = 8.2 Hz, *J*₂ = 2 Hz, 1 H), 3.23 (dd, *J*₁ = 8.2 Hz, *J*₂ = 2 Hz, 1 H), 2.80 (m, 1 H), 2.48 (m, 1 H), 2.03 (dt, *J*₁ = 10 Hz, *J*₂ = 2 Hz, 1 H), 1.62–1.86 (m, 2 H), 1.16–1.35 (m, 3 H); ¹³C NMR 87.10, 70.97, 39.37, 38.45, 35.25, 27.93, 27.33 ppm; IR (neat) of mixture, 2940, 2850, 1440, 1300, 1290, 1085 (s) cm⁻¹; mass spectrum for C₇H₁₀OS₃, calcd 205.9894, obsd 205.9884.

Oxidation of 8. A solution of **8** (150 mg, 0.56 mmol) was treated with 120 mg of 80% MCPBA. The crude product was chromatographed over silica gel using pentane–ether (65:35) as eluent to give 50 mg (31%) of **9** (*R_f* 0.53) and 15 mg (10%) of **10** (*R_f* 0.41). For **9**: ¹H NMR δ 7.53 (m, 5 H), 3.70 (d, *J* = 1.5 Hz, 1 H), 2.98 (d, *J* = 4.3 Hz, 1 H), 2.92 (d, *J* = 4.3 Hz, 1 H), 2.45 (d, *J* = 10.7 Hz, 1 H), 1.75 (m, 1 H), 1.55 (m, 2 H), 1.25 (m, 1 H), 1.10 (m, 1 H); ¹³C NMR 141.07 (s), 127.65 (d), 127.43 (2 C), 86.76 (d), 75.14 (s), 46.36 (d), 40.06 (d), 36.37 (t), 27.34 (t), 25.21 (t) ppm; IR (neat) 3050, 2950, 1440, 1300, 1080 (s), 900, 650, 630, 600 cm⁻¹. Anal. Calcd for C₁₃H₁₄OS₃: C, 55.3; H, 5.0; S, 34.0. Found: C, 55.6; H, 5.1; S, 34.0. For **10** (**9** was always present as an impurity): ¹H NMR δ 7.30 (m, 5 H), 3.80 (d, 1 H), 3.20 (m, 1 H), 2.80 (m, 1 H), 2.40 (d, *J* = 10.7 Hz, 1 H), 1.60 (m, 2 H), 1.50 (d, *J* = 10 Hz, 1 H), 1.20 (m, 1 H), 1.00 (m, 1 H); ¹³C NMR 141.34, 128.65, 128.47, 127.54, 87.91, 87.00, 43.62, 39.92, 37.26, 26.55, 24.64 ppm; IR (neat) 3050, 2950, 2700, 1440, 1300, 1090 (s), 750, 700 cm⁻¹.

Potassium Permanganate (KMnO₄) Oxidation of 5 and 6. To 100 mg (0.5 mmol) of a mixture of **5** and **6** in 5 mL of water containing 100 mg of magnesium sulfate was slowly added a solution of 60 mg of KMnO₄ in 5 mL of water. Decolorization of the KMnO₄ occurred immediately. The solution was stirred at 25 °C for 2 h. Excess sodium metabisulfite was added, resulting in a colorless solution. This was then extracted twice with 10 mL of CH₂Cl₂. The CH₂Cl₂ was separated, washed with brine, and dried over sodium sulfate. Removal of the solvent gave 20 mg of **5**.

Isomerization of 4. A solution of 50 mg (0.24 mmol) of **4** in 0.5 mL of CDCl₃ was stirred rapidly at 25 °C under an atmosphere of dry oxygen. The reaction was followed by ¹H NMR. After 7 days the solution showed an equal mixture of **4** and **7**. The solvent was removed under reduced pressure and the mixture chromatographed over silica gel with pentane–ether (65:35) as eluent to give 20 mg of **4** (*R_f* 0.32) and 20 mg of **7** (*R_f* 0.47). For **7**: mp 81–84 °C; ¹H NMR δ 4.80 (d, *J* = 2 Hz, 2 H), 2.60 (m, 2 H), 2.50 (dt, *J*₁ = 10.6 Hz, *J*₂ = 2 Hz, 1 H), 1.70 (m, 2 H), 1.38 (m, 3 H); ¹³C NMR 79.70 (d), 45.43 (d), 32.57 (t), 27.53 (t) ppm; IR (neat) 2950, 1440, 1310, 1290, 1090 (s) cm⁻¹; mass spectrum for C₇H₁₀OS₃, calcd 205.9893, obsd 205.9893.

Ozonation of 3. A solution of **3** (80 mg, 0.42 mmol) in CH₂Cl₂ (5 mL) was cooled to –78 °C. The solution was saturated with ozone with vigorous stirring. The ozone flow was stopped, and the solution was allowed to warm to 25 °C in the presence of excess ozone. The solvent was removed under reduced pressure and the dark brown gum chromatographed over silica gel with pentane–ethyl acetate (4:1) as eluent to give 20 mg of **7** (*R_f* 0.52) and 30 mg of **4** (*R_f* 0.42). Spectral data of the products were identical with those reported above. The combined yield was 57%.

In a separate experiment 190 mg (1 mmol) of **3** was ozonized at –78 °C and the excess ozone removed by nitrogen bubbling. Upon workup and chromatography, 130 mg (63%) of **4** was obtained as the only product.

Oxidation of 8. A solution of **8** (130 mg, 0.49 mmol) in CH₂Cl₂ (10 mL) was cooled to –78 °C. The solution was then saturated with ozone. The excess ozone was removed by nitrogen bubbling and the solution

warmed to 25 °C. The light yellow oil obtained after removal of solvent was chromatographed over silica gel with pentane–ether (65:35) as eluent to give **9** (60 mg) and **10** (20 mg). The combined yield was 57%.

Preparation of 4 and 7 from Dithiol 17¹⁸ and SOCl₂. A solution of dithiol **17** (160 mg, 1 mmol) and pyridine (80 mg, 1 mmol) in ether (5 mL) was added dropwise during 15 min to a cold (0 °C) well-stirred solution of 120 mg (1 mmol) of SOCl₂ in ether (5 mL). The solution was stirred for another 15 min. The reaction mixture was transferred to separatory funnel and washed with water (2 × 5 mL) and 0.1 M sodium hydroxide (2 × 5 mL) followed with brine. Removal of the ether under vacuum gave 90 mg (44%) of a colorless oil. ¹H and ¹³C NMR analysis of the oil indicated that **4** and **7** were the only products (**4**:**7** = 1.88).

Preparation of 2-Phenylnorbornane-2,3-dithiol (18). To a solution of **8** (300 mg, 1.13 mmol) in 20 mL of dry ether was slowly added 1.5 mL of a 1 M solution of LiAlH₄ in ether under an argon atmosphere. The reaction mixture was stirred at 25 °C for 15 h. The reaction was quenched by slowly adding 25 mL of ice-cold aqueous (5%) HCl. The ether layer was separated, washed with water and brine, and dried over sodium sulfate. Removal of the ether under reduced pressure gave 250 mg (88%) of **18** as a colorless oil: ¹H NMR δ 7.15–7.50 (m, 5 H), 3.35 (d, 1 H), 2.95 (s, 1 H), 2.32 (m with a s, 4 H), 1.48 (m with a s, 4 H), 1.16 (m, 1 H); ¹³C NMR 147.24, 128.54, 126.51 (2 C), 63.95, 52.87, 50.32, 49.76, 35.52, 29.94, 24.37 ppm; IR (neat) 3010, 2910, 2490 (w, SH str), 1445, 1320, 1170, 760, 700 cm⁻¹.

Preparation of 19 and 20. A solution of **18** (240 mg, 1 mmol) and pyridine (80 mg, 1 mmol) in ether (5 mL) was added dropwise to a cold (0 °C) well-stirred solution of SOCl₂ (120 mg, 1 mmol) in ether (5 mL). After the addition the solution was stirred for 15 min. It was then washed with water and 0.1 M sodium hydroxide solution. After being washed with brine, the ether layer was dried over sodium sulfate and the solvent removed under reduced pressure to give **19** and **20** as a white solid. Trituration of the mixture with pentane gave 110 mg (39%) of pure **19** as the residue. Removal of the pentane under reduced pressure gave 30 mg (11%) of **20** as a viscous oil. For **19**: mp 130–131 °C; ¹H NMR δ 7.40 (m, 5 H), 4.65 (d, *J* = 1.5 Hz, 1 H), 3.25 (m, 1 H), 2.90 (d, *J* = 11.7 Hz, 1 H), 2.75 (m, 1 H), 1.75 (series of m, 2 H), 1.63 (d, *J* = 11.7 Hz, 1 H), 1.45 (m, 1 H), 1.35 (m, 1 H); ¹³C NMR 140.19, 129.09, 128.19, 126.08, 100.75, 80.29, 48.20, 47.33, 35.61, 29.46, 24.55 ppm; IR (KBr) 2900, 1440, 1080, 750, 700 cm⁻¹. Anal. Calcd for C₁₃H₁₄OS₂: C, 55.3; H, 5.0; S, 34.0. Found: C, 55.0; H, 4.9; S, 34.3. For **20**: ¹H NMR δ 7.40 (m, 5 H), 5.08 (d, *J* = 1.5 Hz, 1 H), 3.13 (m, 1 H), 2.50 (m, 1 H), 2.40 (d, *J* = 11.7 Hz, 1 H), 1.75 (series of m, 2 H), 1.50 (d, *J* = 11.7 Hz, 1 H), 1.45 (m, 1 H), 1.35 (m, 1 H); ¹³C NMR 143.79, 128.68, 127.43, 127.23, 94.71, 75.98, 47.78, 45.29, 34.66, 27.07, 23.72 ppm; IR (neat) 3050, 2950, 1440, 1260, 1100, 740 cm⁻¹.

Reaction between 8 and Norbornene. A solution of **8** (80 mg, 0.3 mmol) and norbornene (30 mg, 0.32 mmol) in 0.75 mL of benzene-*d*₆ was sealed under air in a 5-mL vial. The vial was immersed in an oil bath kept at 102 °C for 12 h. After cooling, the contents of the flask were transferred into a 5-mm NMR tube and the solution was analyzed. No signals for **8** or norbornene were observed in either the ¹H NMR or ¹³C NMR spectra. On the other hand, the absorptions could be easily attributed to the very well characterized **3** and 2-phenyl-2-norbornene. An upfield shift for the H₂ and H₃ protons of **3** from δ 3.60 (CDCl₃) to δ 3.20 in benzene-*d*₆ was observed. Integrating the peak at δ 6.00 for 2-phenyl-2-norbornene and at δ 3.20 for **3** showed that both the components were present in equal amounts.

Reaction between 8 and Norbornadiene. A mixture of **8** (270 mg, 1.0 mmol) and norbornadiene (100 mg, 1.1 mmol) in 2.5 mL of benzene was heated in a sealed tube at 102 °C for 6 h. The crude material obtained after removal of the solvent under reduced pressure was chromatographed over silica gel with petroleum ether as eluent. The components isolated in order of decreasing *R_f* values were 2-phenyl-2-norbornene (120 mg, 71%), **21**¹ (80 mg, 43%), and **8** (70 mg, 26%).

Preparation of 2-Carbomethoxy-2-norbornene (24). A solution of **26** (200 mg, 1.33 mmol) in 10 mL of ethyl acetate containing 10 mg of Pd on charcoal was carefully hydrogenated by using a small rubber balloon filled with hydrogen. The reaction was stopped when 85% of **24** had formed. Any further hydrogenation resulted in complete saturation. The catalyst was filtered and the solvent removed under reduced pressure. This gave 250 mg of a colorless oil containing 85% of **24**. This was used for the transfer reaction without further purification: ¹H NMR δ 6.90 (d, 1 H), 3.25 (s, 3 H), 3.28 (m, 1 H), 3.00 (m, 1 H), 1.75 (series of m, 2 H), 1.50 (d, 1 H), 1.25 (series of m, 2 H), 1.08 (d, 1 H); ¹³C NMR 165.20, 146.86, 140.68, 51.14, 48.13, 43.43 ppm.

Reaction of 24 with 8. A solution of **24** (100 mg containing 15% of **26**) and **8** (135 mg, 0.5 mmol) in 1.5 mL of benzene in a sealed tube was heated at 100 °C for 24 h. The dark oil obtained after removal of benzene under reduced pressure was chromatographed over silica gel with

pentane-CH₂Cl₂ (1:1) as eluent. The compounds isolated in order of increasing R_f values were **24** (30 mg), **25** (70 mg), **8** (20 mg), and 2-phenyl-2-norbornene (20 mg). For **25**: mp 80–81 °C; ¹H NMR δ 4.20 (d, $J = 2.1$ Hz, 1 H), 3.75 (s, 3 H), 2.78 (m, 1 H), 2.40 (m, 1 H), 2.20 (d, $J = 10.7$ Hz, 1 H), 1.75 (m, 2 H), 1.20 (m, 3 H); ¹³C NMR 171.98 (s), 83.90 (s), 68.88 (d), 52.88 (q), 44.04 (d), 41.66 (d), 34.19 (t), 26.70 (t), 25.08 (t) ppm; IR (neat) 2950, 1720, 1420, 1250, 1218, 1010, 760 cm⁻¹; mass spectrum for C₉H₁₂O₂S₃, calcd 247.9999, obsd 247.9988. Yield of **25** based on recovered **8** was 68%.

Reaction of 26 with 8. A solution of **8** (130 mg, 0.49 mmol) and **26** (80 mg, 0.53 mmol) in benzene (1 mL) was heated in a sealed tube at 100 °C for 12 h. The benzene was removed under reduced pressure, and the crude material was chromatographed over silica gel with pentane-ether (9:1) as eluent. The compounds isolated in order of increasing R_f were **26** (20 mg), **27**, and **28** as a mixture (45 mg, 40% based on recovered **8**), **8** (20 mg), and 2-phenyl-2-norbornene (40 mg). The mixture of **27** and **28** was separated by a second chromatography over silica gel with pentane-CH₂Cl₂ (1:1) as eluent to give **28** (R_f 0.31, 20 mg) and **27** (R_f 0.51, 20 mg). For **28**: ¹H NMR δ 7.20 (d, $J = 3.1$ Hz, 1 H), 4.10 (AB q, $J_1 = 18.1$ Hz, $J_2 = 1.9$ Hz, 2 H), 3.78 (s, 3 H), 3.30 (m, 1 H), 3.08 (m, 1 H), 2.60 (d, $J = 9.8$ Hz), 1.85 (d, $J = 9.8$ Hz, 1 H); ¹³C NMR 164.00, 149.22, 145.00, 69.80, 69.42, 57.80, 47.93, 46.67, 43.14 ppm; IR (neat) 2925, 1700, 1585, 1420, 1260, 1150, 1080, 760 cm⁻¹; mass spectrum for C₉H₁₀O₂S₃, calcd 245.9844, obsd 245.9850. For **27**: ¹H NMR δ 6.45 (m, 1 H), 6.35 (m, 1 H), 4.55 (d, $J = 2.3$ Hz, 1 H), 3.75 (s, 3 H), 3.20 (m, 1 H), 2.85 (m, 1 H), 2.65 (d, $J = 9.8$ Hz, 1 H), 1.85 (d, $J = 9.8$ Hz, 1 H); ¹³C NMR 172.03, 139.81, 137.66, 86.09, 72.24, 52.81, 48.43, 46.32, 44.66 ppm; IR (neat) 2945, 1720, 1420, 1030, 700 cm⁻¹; mass spectrum for C₉H₁₀O₂S₃, calcd 245.9843, obsd 245.9842.

Competitive Trithiane Transfer. (i) A solution of **8** (70 mg, 0.26 mmol), norbornene (30 mg, 0.32 mmol), and norbornadiene (30 mg, 0.33 mmol) in 0.6 mL of benzene-*d*₆ was heated in a sealed tube at 101 °C for 6 h. After cooling, the contents of the tube were analyzed by ¹H NMR. The relative amounts of **3** and **21** were determined by integrating the doublets at δ 3.20 (for **3**) and δ 3.40 (for **21**). The ratio **3:21** = 1.35. (ii) In a similar experiment 57.3 mg (0.22 mmol) of **8**, 21.7 mg (0.23 mmol) of norbornene, and 32.7 mg (0.23 mmol) of benzonorbornadiene was heated in 0.3 mL of benzene-*d*₆ for 6.5 h, and the contents were

analyzed by ¹H NMR. Since the absorption of the bridgehead protons of **29** and H₂, H₆ of **3** overlap in benzene-*d*₆, the benzene was removed under reduced pressure and the oil redissolved in CDCl₃. The relative amounts of **3** and **29** were determined by integrating the doublets at δ 3.60 (for **3**) and δ 3.98 (for **29**). The ratio of **3:29** = 1.56. (iii) In a similar experiment 51.8 mg (0.19 mmol) of **8**, 18.2 mg (0.19 mmol) of norbornene, and 21.7 mg (0.2 mmol) of 2-methyl-2-norbornene were heated for 6.5 h. Analysis of the mixture by ¹H NMR indicated **3** and unreacted **8**.

9 as a Transfer Reagent. A mixture of **9** (60 mg, 0.21 mmol) and norbornene (30 mg, 0.32 mmol) in 1 mL of benzene was heated in a sealed tube at 100 °C for 12 h. The dark oil obtained after removal of unreacted norbornene and benzene under reduced pressure was chromatographed over silica gel with pentane-ether (65:35) as eluent to give a mixture of **5** and **6** (20 mg), 2-phenyl-2-norbornene (20 mg), and 20 mg of a viscous yellow oil that could not be characterized. The ratio **5:6** as determined by ¹H NMR was 2.7.

10 as a Transfer Reagent. An identical experiment as described above was carried out with **10** (40 mg) and norbornene (20 mg). After heating, the unreacted norbornene and benzene was removed under reduced pressure. ¹H NMR analysis of the oil showed **5**, **6**, and 2-phenyl-2-norbornene. The ratio **5:6** was 2.4.

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Registry No. **3**, 23657-27-4; **4**, 116376-52-4; **5**, 116376-53-5; **6**, 116497-38-2; **7**, 116497-40-6; **8**, 109909-04-8; **9**, 116376-54-6; **10**, 116497-39-3; **17**, 23657-28-5; **18**, 116376-55-7; **19**, 116376-56-8; **20**, 116497-41-7; **21**, 109958-15-8; **24**, 701-15-5; **25**, 116376-57-9; **26**, 3604-36-2; **27**, 116376-58-0; **28**, 116376-59-1; 2-phenyl-2-norbornene, 4237-08-5.

Supplementary Material Available: Experimental details and data for S₃-transfer kinetics (4 pages). Ordering information is given on any current masthead page.

High Intrinsic Rate Constant and Large Imbalances in the Thiolate Ion Addition to Substituted α -Nitrostilbenes¹

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Abstract: The kinetics of the reversible addition of alkyl thiolate ions (RS⁻ with R = Et, HOCH₂CH₂, CH₃OCOCH₂CH₂, and CH₃OCOCH₂) to α -nitrostilbene and of HOCH₂CH₂S⁻ to α -nitrostilbene substituted in the α -phenyl ring (Z = 4-CH₃, H, 4-Br, 3-NO₂, and 4-NO₂) have been measured in 50% Me₂SO–50% water at 20 °C. Brønsted β values (β_{nuc} , $\beta_{1\text{g}}$, β_{eq}), Hammett ρ values ($\rho(k_1)$, $\rho(k_{-1})$, $\rho(K_1)$), and the intrinsic rate constant ($k_0 = k$ when $K = 1$) have been determined and compared with the corresponding parameters for piperidine and morpholine addition to the same substrates reported previously. For a given pK_a of the nucleophile, thiolate ion addition is thermodynamically and kinetically much more favorable than amine addition, presumably because of soft–soft type interactions both in the adduct and in the transition state. The fact that the *intrinsic* rate for thiolate ion addition is also much higher than for amine addition implies that the soft–soft interactions in the transition state have progressed more than bond formation. The structure–reactivity coefficients indicate a strongly imbalanced transition state in which development of resonance and solvation at the α -nitro group lags behind carbon–sulfur bond formation. Rate constants for carbon protonation of the HOCH₂CH₂S⁻ adducts of the substituted α -nitrostilbenes by acetic acid were also determined. They are correlated by a *positive* Hammett ρ value of 0.33, indicating that electron-withdrawing substituents enhance the rate. This unusual substituent dependence is reminiscent of the nitroalkane anomaly reported for phenylnitroalkanes.

The kinetics and mechanism of amine and oxyanion addition to activated olefins have received a great deal of attention in recent years,^{1,2} and much has been learned about structure–reactivity relationships in these reactions as well as carbanion-forming processes in general.³

In contrast, much fewer reports about reactions of thiols or thiolate ions at C=C double bonds have appeared. An early series of rate and equilibrium studies involved the reaction of 1-butanethiol with benzylidene-1,3-indandiones, benzylideneacetyl-

(1) This is part 23 in the series *Nucleophilic Addition to Olefins*. Part 22: Bernasconi, C. F.; Bunnell, R. D. *J. Org. Chem.* **1988**, *53*, 2001.

(2) Parts 1–21 in this series.

(3) Reviews: (a) Bernasconi, C. F. *Pure Appl. Chem.* **1982**, *54*, 2335. (b) Bernasconi, C. F. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry 215; American Chemical Society: Washington, DC 1987; p 137.