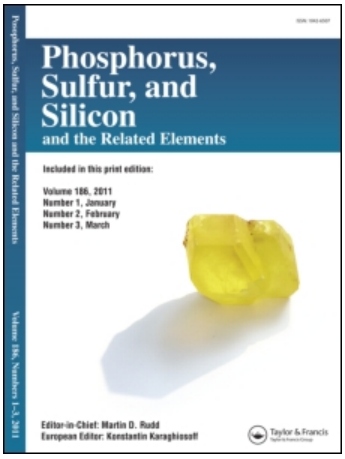

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STEREOSELECTIVITY OF OXIDATION OF 2-SUBSTITUTED-1,3-DITHIOLANES

Francis A. Carey[a]; Oliver D. Dailey Jr.[a]; Thomas E. Fromuth[a]
[a] Department of Chemistry, University of Virginia, Charlottesville, Virginia

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STEREOSELECTIVITY OF OXIDATION OF 2-SUBSTITUTED-1,3-DITHIOLANES

FRANCIS A. CAREY*, OLIVER D. DAILEY, JR., and THOMAS E. FROMUTH

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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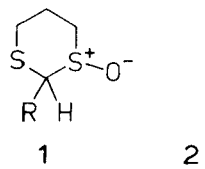
The stereoselectivity of oxidation of 2-methyl-1,3-dithiolane (**3**), 2-phenyl-1,3-dithiolane (**7**), and 2-*tert*-butyl-1,3-dithiolane (**15**) with sodium metaperiodate and with *m*-chloroperoxybenzoic acid affords primarily the *trans*-1-oxide corresponding to attack from the less-hindered side. The trans/cis ratio varies from 3/2 for oxidation of **3** to cleanly *trans* for **15**. Further oxidation of 1,3-dithiolane 1-oxides produces *trans*-1,3-dioxides. The ^{13}C NMR spectra of the oxidation products provide valuable clues for stereochemical determination.

INTRODUCTION

As a continuation of our work on the stereochemical properties of sulfoxides derived from heterocycles containing two or more sulfur atoms,[1] we have examined the synthesis and some reactions of 2-substituted-1,3-dithiolane 1-oxides. While a relatively clear picture has emerged concerning the stereochemistry, particularly the conformations, of 1,3-dithiane 1-oxides (**1**),[2] the situation in their five-membered counterparts has received less attention. The only previous work relative to the stereochemistry of monosulfoxides derived from 1,3-dithiolanes is that of Chen[3] who studied their thermal rearrangement reactions. He found that *m*-chloroperoxybenzoic acid oxidation of 2-methyl-2-substituted-1,3-dithiolanes (**2**, R = alkyl, aryl, or aralkyl) occured *trans* to the substituent R, i.e., from the less hindered side. Oxidation of 2-methyl-1,3-dithiolane (**3**), gave a 7:3 mixture of sulfoxides in which the major diastereomer (δ_{CH_3} 1.53 ppm) was shown to be *trans*-2-methyl-1,3-dithiolane 1-oxide (**4**) and the minor diastereomer (δ_{CH_3} 1.65 ppm) was *cis*-2-methyl-1,3-dithiolane 1-oxide (**5**). The invididual diastereomers **4** and **5** were not separated in Chen's study but were subjected to thermolysis as a mixture. Their structures were deduced on the basis of the reasonable assumption that only the *cis*-oxide **5** can rearrange to the observed dihydro-1,4-dithiin (**6**) while the *trans*-oxide **4** is stable to thermolysis.



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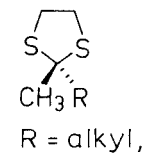
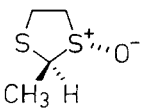


2 R = alkyl, aryl
3 R = H



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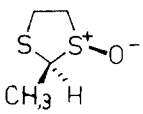

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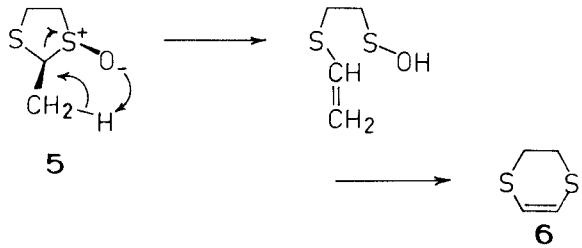


5 **6**

RESULTS

Oxidations of 2-substituted-1,3-dithiolanes were carried out with the customary reagents; *m*-chloroperoxybenzoic acid and sodium metaperiodate. The oxidation of 2-methyl-1,3-dithiolane (**3**) with sodium metaperiodate proceeded with a stereoselectivity similar to that observed by Chen[4] for the peroxyacid oxidation of **3**. A mixture of diastereomers was isolated in 94% yield in which the *trans-cis* ratio **4**/**5** was 3:2 as estimated by ^1H NMR. Preparative thin-layer chromatography afforded the pure diastereomers. The major diastereomer **4** exhibited its

TABLE I

^{13}C Chemical shifts of 1,3-dithiolanes and 1,3-dithiolane oxides

Compound	M[c]	Chemical shift, δ[a,b] C(2)	C(4)	C(5)
1,3-dithiolane (**10**)	1.00	34.2	38.0	38.0
2-methyl-1,3-dithiolane (**3**)[d]	1.00	48.0	39.0	39.0
2-phenyl-1,3-dithiolane (**7**)[e]	1.00	56.0	40.0	40.0
2-*tert*-butyl-1,3-dithiolane (**15**)[f]	1.00	66.4	39.1	39.1
1,3-dithiolane 1-oxide (**11**)	1.00	56.8 (22.6)	31.1 (−6.9)	54.9 (16.9)
trans-2-methyl-1,3-dithiolane 1-oxide (**4**)[g]	1.00	66.7 (18.7)	31.1 (−7.9)	53.7 (14.7)
trans-2-phenyl-1,3-dithiolane 1-oxide (**8**)[h]	1.00	77.3 (21.3)	32.1 (−7.9)	52.8 (12.8)
trans-2-tert-butyl-1,3-dithiolane 1-oxide (**16**)[i]	0.40	89.7 (23.3)	32.7 (−6.4)	57.0 (17.9)
cis-2-methly-1,3-dithiolane 1-oxide (**5**)[j]	1.00	62.1 (14.1)	31.3 (−7.7)	56.2 (17.2)
cis-2-phenyl-1,3-dithiolane 1-oxide (**9**)[k]	1.00	71.7 (15.7)	32.0 (−8.0)	56.4 (16.4)
1,3-dithiolane *trans*-1,3-dioxide (**18**)	0.58	78.3 (44.1)	52.0 (14.0)	52.0 (14.0)
cis-2-phenyl-1,3-dithiolane *r* − 1, *trans*-3-dioxide (**12**)	0.24	94.9 (38.9)	52.8 (12.8)	53.0 (13.0)
trans-2-phenyl-1,3-dithiolane *r* − 1, *cis*-3-dioxide (**13**)	0.17	92.8 (36.8)	50.2 (10.2)	50.2 (10.2)

[a] Chemical shifts are in ppm from internal TMS.

[b] $\Delta\delta$ Values are in parentheses and are defined as δ_{oxide}-δ_{parent} dithiolane. A positive value indicates the carbon atom of the 1,3-dithiolane 1-oxide appears at lower field (deshielded) than the carbon atom of the corresponding 1,3-dithiolane. A negative sign is indicative of upfield shift (shielding) on oxidation.

A negative sign is indicative of upfield shift (shielding) on oxidation.

[c] Concentration (mol/L) in $CDCl_3$.

[d] CH_3: 24.6 ppm.

[e] Phenyl carbons: 127.7, 128.2, 128.7, and 133.3 ppm.

[f] CH_3: 27.5; C: 36.6 ppm.

[g] CH_3: 18.3 ppm.

[h] Phenyl carbons: 128.1, 128.6, and 132.8 ppm.

[i] CH_3: 28.4; C: 34.2 ppm.

[j] CH_3: 12.9 ppm.

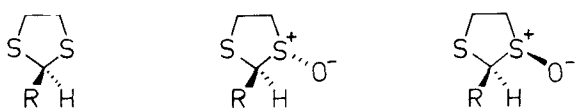
[k] Phenyl carbons: 128.2, 129.0, 129.4, and 130.2 ppm.

methyl signal at δ 1.48 ppm and the minor diastereomer at δ 1.63 ppm in good agreement with Chen's observations.

The ^{13}C NMR spectra of the isolated oxides provide further evidence in support of their stereochemical assignments (Table I). The methyl carbon resonance of the *cis* oxide **5** is significantly more shielded (12.9 ppm) than that of the *trans* oxide **4** (18.3 ppm). Shielding of methyl by the γ-oxygen substituent should be greater when they are *cis* than when they are *trans* by analogy to the chemical shifts of substituted methylcyclopentanes.[4]

In examining the chemical shifts for the ring carbons of **4** and **5** relative to the parent 2-methyl-1,3-dithiolane (**3**), one finds that the substituent effect of oxygen ($\Delta\delta = \delta_{sulfoxide} - \delta_{parent}$) is greater at C(2) than at C(5) in the *trans*-oxide **4** (18.7 *vs.* 14.7 ppm) but less at C(2) than at C(5) in the *cis* oxide **5** (14.1 *vs.* 17.2 ppm). An upfield shift at C(4) is observed on oxidation, the magnitude of which is comparable in the two diastereomers ($\Delta\delta = -7.7$ and -7.9 ppm).

Oxidation of 2-phenyl-1,3-dithiolane (**7**) with sodium metaperiodate or with *m*-chloroperoxybenzoic acid is stereoselective and gives predominantly the same diastereomer in both cases. The peroxyacid oxidation is highly stereoselective: analysis of the crude reaction mixture



7 R = Ph **8** R = Ph **9** R = Ph

10 R = H **11** R = H

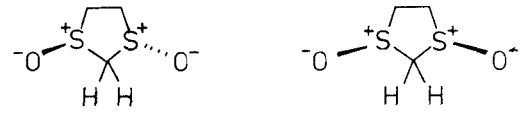
15 R = $(CH_3)_3C$- **16** R = $(CH_3)_3C$-

17 R = $(CH_3)_3C$-

from duplicate runs indicated almost exclusive formation of a single diastereomer, presumably *trans*-2-phenyl-1,3-dithiolane 1-oxide (**8**). On a preparative scale, **8** was isolated in 80% yield along with 10% of *cis*-2-phenyl-1,3-dithiolane 1-oxide (**9**). The degree of stereoselectivity associated with periodate oxidation was more variable from experiment to experiment with ratios of **8**/**9** ranging from 2.5:1 to 7:1 by NMR analysis. In a preparative experiment, the major diastereomer **8** was isolated in 79% yield and the minor diastereomer in 5% yield. Stereochemical assignments of **8** and **9** may be made by assuming that peroxyacid oxidation of **7** occurs *trans* to the phenyl substituent by analogy with Chen's observations and that periodate behaves similarly by analogy to the results just obtained with **3**. Thus, **8** should be the major diastereomer and **9** the minor one.

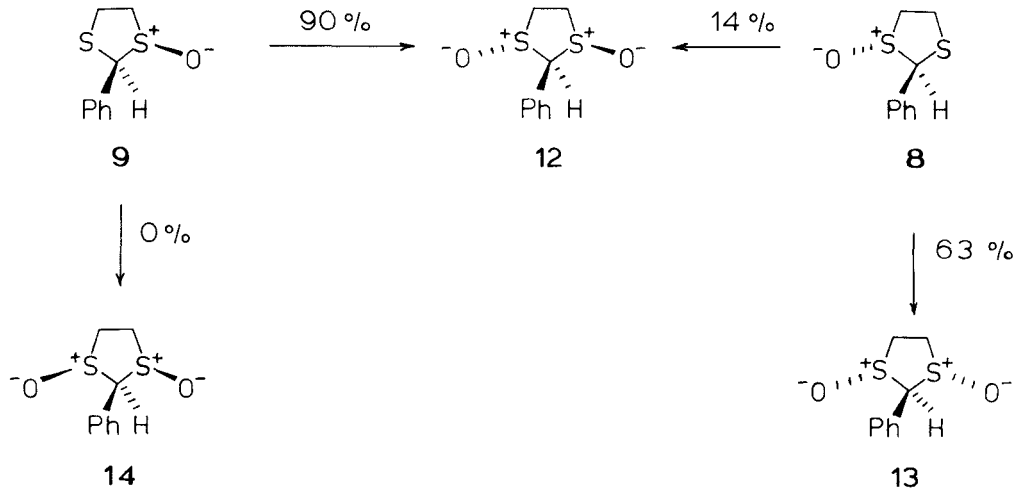
These conclusions are supported by the ^{13}C NMR spectra of the individual diastereomers which follow the pattern of shifts observed in **4** and **5** (Table I). The substituent effect of oxygen ($\Delta\delta$) is observed to be greater at C(2) than at C(5) in the major diastereomer (21.3 *vs.* 12.8 ppm) and less at C(2) than at C(5) in the minor diastereomer (15.7 vs. 16.4 ppm).

Additional evidence in support of these assignments can be found in experiments in which 1,3-dithiolanes and their 1-oxides are oxidized to 1,3-dioxides. Oxidation of 1,3-dithiolane (**10**) with two equivalents of *m*-chloroperoxybenzoic acid or of 1,3-dithiolane 1-oxide (**11**) with sodium metaperiodate affords 1,3-dithiolane *trans*-1,3-dioxide (**18**)[5] as the exclusive product in >90% yield. The stereoselectivity of oxidation may be deduced from the ^1H NMR spectrum of the compound in which the protons at C(2) appear as isochronous nuclei. The C(2) protons of the *trans*-1,3-dioxide (**18**) are enantiotopic and therefore must have the same chemical shift while the C(2) protons of the *cis*-1,3-dioxide (**19**) are diastereotopic and would be expected to have different chemical shifts. In order to verify that the chemical shift equivalence of the protons at C(2) in the product was indeed a result of their enantiotopic relationship, the NMR spectrum was measured in the presence of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium[Eu(fod)$_3$]. At the concentrations of Eu(fod)$_3$ employed, the C(2) protons experience a downfield shift of ca. 1.5 ppm but remain isochronous. If the 1,3-dioxide were *cis* with accidental chemical shift equivalence between the C(2) protons, it is unlikely that the accidental equivalence would persist in the presence of coordination of a sulfoxide oxygen to europium. Thus, we conclude that the stereochemical preference for formation of *trans*-1,3-dioxides from 1,3-dithiolanes is high.



18 **19**

When the stereisomeric 2-phenyl-1,3-dithiolane 1-oxides **8** and **9** were subjected to further oxidation (Scheme I) it was found that treatment of the minor diastereomer **9** with *m*-chloroperoxybenzoic



SCHEME I Oxidation of diastereomeric 2-phenyl-1,3-dithiolane 1-oxides with *m*-chloroperoxybenzoic acid.

acid afforded a single 1,3-dioxide **12** in 90% yield. The *trans* relationship of the two oxygen substituents in **12** follows from its ^{13}C NMR spectrum which shows C(4) and C(5) to be nonequivalent, although very similar in chemical shift (53.0 and 52.8 ppm). Of the three possible diastereomeric 2-phenyl-1,3-dithiolane 1,3-dioxides (**12**, **13**, and **14**), C(4) and C(5) are diastereotopic only in **12**. When the oxidation of the major diastereomer **8** was performed, a mixture of disulfoxide **12** (14% isolated yield) and a *meso*-disulfoxide (**13**) (63% isolated yield) was obtained and separated by preparative thin-layer chromatography. The ^{13}C NMR spectrum of **13** showed the enantiotopic carbons C(4) and C(5) as equivalent. While compound **12** can be, and is, formed by oxidation of either **8** or **9**, it is more reasonable to conclude that it is the major product from **9** and the minor product from **8** rather than *vice versa*. Similarly, it is more reasonable to conclude that the *meso*-disulfoxide which is absent from the products is the all-*cis* 1,3-dioxide **14** rather than **13**.

When 2-*tert*-butyl-1,3-dithiolane 1-oxide (**15**) was oxidized with *m*-chloroperoxybenzoic acid, sodium metaperiodate, or hydrogen peroxide only a single diastereomeric 1-oxide was formed. The ^{13}C NMR spectrum of this material indicated that, relative to dithiolane **15**, C(2) underwent a downfield shift of 23.3 ppm and C(5) a downfield shift of 17.9 ppm in accordance with its formulation as *trans*-2-*tert*-butyl-1,3-dithiolane 1-oxide (**16**).

DISCUSSION

As was previously observed with 2-substituted-1,3-dithianes,[6] the oxidation of 1,3-dithiolanes with either *m*-chloroperoxybenzoic acid or with sodium metaperiodate affords primarily the *trans* 1-oxide. In contrast to the 1,3-dithianes where the *trans*/*cis* ratio was uniformly 9:1 irrespective of the 2-substituent, the stereoselectivity of oxidation of 1,3-dithiolanes ranges from *ca.* 3:2 in the oxidation of **3** to essentially quantitative formation of the *trans*-oxide **16** from **15**. These results parallel those reported earlier by Chen[3] who reported similar observations in the peroxyacid oxidations of 2,2-disubstituted-1,3-dithiolanes.

The tendency for oxygen transfer *trans* to substituents on the dithiolane ring is seen as well in oxidation of 1,3-dithiolane 1-oxides to 1,3-dioxides. The *trans*-1,3-dioxide is formed exclusively from 1,3-dithiolane (**10**) via **11** and from *cis*-2-phenyl-1,3-dithiolane 1-oxide (**9**) where the second oxygen can add *trans* to both substituents already present. In the case of *trans*-2-phenyl-1,3-dithiolane 1-oxide (**8**) the effect of the 2-phenyl substituent dominates and oxygen is transferred preferentially *trans* to it (*cis* to the sulfoxide oxygen), but by a smaller amount (63:14).

Disubstitution at C(2) leads, apparently, to non-stereoselective formation of 1,3-dioxides. Kuhn and Neugebauer[7] have reported, and we have confirmed,[8] that 2,2-diphenyl-1,3-dithiolane gives comparable quantities of the *cis* and *trans*-1,3-dioxides on oxidation with hydrogen peroxide in acetic acid.[9]

Attention is drawn to the utility of ^{13}C NMR in determining sulfoxide stereochemistry. As was the case with 1,3-dithiane 1-oxides,[2a] the signal for C(2) is shifted to lower field in the *trans*-2-substituted sulfoxides than in the cis. Based on the data presented here, it appears that the 2-substituted-1,3-dithiolane 1-oxides can have their configurations assigned, even if only one is available and no direct comparisons can be made between diastereomers, by noting the relative shifts of C(2) and C(5). In the *trans*-oxides the downfield shift $\Delta\delta$ is 4–8 ppm greater at C(2) than at C(5) while in the *cis*-oxides the downfield shift $\Delta\delta$ is slightly larger at C(5) than at C(2).

EXPERIMENTAL SECTION

Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrometer as KBr disks or thin films. Melting points and boiling points are uncorrected. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Proton NMR spectra were obtained at 90 MHz on a Varian EM-390 or at 60 MHz on a Hitachi Perkin-Elmer R-20 spectrometer. Carbon 13 NMR spectra were recorded using a JEOL-PS 100 P/EC-100 Fourier transform spectrometer. The operating conditions are described in reference 2a.

2-substituted-1,3-dithiolanes **3**, **7**, *and* **15** were prepared in the usual manner by reaction of 1,2-ethanedithiol with the appropriate aldehyde in chloroform saturated with hydrogen chloride. Each of these compounds **3**,[11] **7**,[12] and **15**[13] have been previously reported and their ^{1}H and ^{13}C NMR spectra were consistent with the proposed structures.

Oxidation of 2-substituted-1,3, dithiolanes. Typical oxidation conditions are presented in detail for the case of 2-phenyl-1,3-dithiolane (**7**). The analogous reactions of **3** and **15** were performed in a similar fashion.

Oxidation of 2-phenyl-1,3-dithiolane (**7**) *with m-chloroperoxybenzoic acid.* A solution of 3.05 g (15.0 mmol) of 85% MCPBA in 75 ml of dichloromethane was added dropwise to a solution

of **7** (2.73 g, 15.0 mmol) in 50 ml of dichloromethane over a 1 hr period at −15 to −10°C. After storage at −25°C overnight, the mixture was washed with 100 ml of 10% aqueous sodium carbonate and 100 ml of brine and dried over sodium sulfate. Removal of solvent afforded 3.00 g of clear colorless oil. The NMR spectrum showed 89% *trans*-2-phenyl-1,3-dithiolane 1-oxide (**8**) and 11% *cis*-2-phenyl-1,3-dithiolane 1-oxide (**9**). A 2.48 g portion of product was loaded on a column containing 20 g of Silica Gel 60. Elution with 2.5% 2-propanol/carbon tetrachloride provided 1.56 g of **8**, mp 62.5–64°C, and 522 mg of a mixture of **8** and **9**. Further elution with 7% 2-propanol/carbon tetrachloride gave 266 mg of **8** plus **9**. Preparative TLC (silica gel; 15% 2-propanol/carbon tetrachloride) of the mixtures afforded 398 mg of **8** (R_f 0.27) and 255 mg of **9** (mp 75.5–77°C, R_f 0.16). The isolated yields of **8** and **9** therefore totaled 1.96 g (80%) and 0.26 g (10%), respectively. Recrystallization of **8** from 4:1 ether-dichloromethane gave the analytical sample: mp 66–67°C; IR(KBr) 1035 cm^{-1} (S = O); ^1H NMR ($CDCl_3$) δ 2.6–4.0 (m, 4, CH_2CH_2), 5.38 (s, 1, C-2 H), and 7.3–7.7 ppm (m, 5, arom).

Anal. Calcd. for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 54.50; H, 5.11; S, 32.30.

Recrystallization of **9** from cyclohexane gave the analytical sample: mp 91–92°C; IR(KBr) 1045 cm^{-1} (S = O); ^1H NMR ($CDCl_3$) δ 2.8–4.2 (m, 4, CH_2CH_2), 5.29 (s, 1, C-2 H), and 7.2–7.7 ppm (m, 5, Ph).

Anal. Calcd. for $C_9H_{10}OS_2$: C, 54.51; H, 5.08, S, 32.34. Found: C, 54.38; H, 5.11; S, 32.19.

Oxidation of 2-phenyl-1,3-dithiolane (**7**) *with sodium metaperiodate.* A solution of 2.80 g (13.1 mmol) of sodium metaperiodate in 30 ml of water was added dropwise to a solution of 2.36 g (13.1 mmol) of **7** in 100 mL of methanol at −15° to −5°C. The resulting stirred at −15° to −5°C for one hour then refrigerated overnight. The precipitated $NaIO_3$ was removed by filtration and washed with methanol, the methanol being combined with the filtrate. The solvents were removed in vacuo. The remaining residue was dissolved in 100 ml $CHCl_3$ and washed with 500 mL brine. The aqueous layer was extracted with $CHCl_3$, and the $CHCl_3$ layers combined. The organic solution was dried (Na_2SO_4) and evaporated leaving 2.30 g of yellow oil. The crude product was chromatographed on 22 g of silica gel and eluted first with 300 mL of CCl_4, then with 2% 2-propanol in CCl_4. Fractions which contained mixtures of diastereomeric oxides were further purified by preparative TLC on silica gel using 15% 2-propanol in CCl_4. There was obtained by this procedure 1.81 g (79%) of *trans*-2-phenyl-1,3-dithiolane 1-oxide (**8**) and 0.11 g (5%) of *cis*-2-phenyl-1,3-dithiolane 1-oxide (**9**).

Oxidation of 2-methyl-1,3-dithiolane (**3**) *with sodium metaperiodate.* A 2.00 g portion (16.7 mmol) of **3** was oxidized with $NaIO_4$ as described above. The crude product (2.12 g, 94%) was a 3:2 mixture of *trans*-2-methyl-1,3-dithiolane (**4**) and *cis*-2-methyl-1,3-dithiolane (**5**) as estimated by ^1H NMR. The crude product was distilled at 81°C and 0.22 Torr and a 353 mg portion of the distillate chromatographed on three silica gel plates using 15% 2-propanol/CCl_4 as developing solvent (seven developments). Extraction of the higher R_f band in 25% ethanol/chloroform gave 212.7 mg of **4**, mp 42–46°C. Recrystallization from cyclohexane provided the analytical sample: mp 48–49°C; IR(KBr) 1050 cm^{-1} (S = O); ^1H NMR ($CDCl_3$) δ 1.48 (d, 3, J = 7 Hz, CH_3), 2.5–3.9 (m, 4, $-CH_2CH_2-$), and 4.16 ppm (q, 1, J = 7 Hz, C-2 H).

Anal. Calcd. for $C_4H_8OS_2$: C, 35.26; H, 5.92; S, 47.07. Found: C, 35.32; H, 5.94; S, 47.01.

Extraction of the lower R_f band furnished 104.7 mg of **5**, mp 41–46°C. The analytical sample was obtained upon recrystallization from cyclohexane: mp 49–51°C; IR(KBr) 1035 (vs) and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (d, 3, J = 7 Hz, CH_3), 2.5–3.9 (m, 4, $-CH_2CH_2-$), and 4.20 ppm (q, J = 7 Hz, C-2 H).

Anal. Calcd. for $C_4H_8OS_2$: C, 35.26; H, 5.92; S, 47.07. Found: C, 32.25; H, 5.95; S, 47.12.

Oxidation of 2-tert-butyl-1,3-dithiolane (**15**) *with m-chloroperoxybenzoic acid.* A 1.68 g sample (10.4 mmol) of **15** was oxidized with *m*-chloroperoxybenzoic acid as described for the case of **7**. The crude product (1.89 g) was a yellow oil which was purified by chromatography on silica gel to give 1.67 g (93%) of *trans*-2-*tert*-butyl-1,3-dithiolane 1-oxide (**16**). The analytical sample was obtained by evaporative distillation at 0.3 Torr (bath temp 50–110°C); ^1H NMR ($CDCl_3$) δ 1.15 (s, 9, CH_3), 2.5–2.9 and 3.2–3.8 (m, 4, CH_2CH_2), and 3.98 ppm (s, 1, C-2 H).

Anal. Calcd. For $C_7H_{14}OS_2$: C, 47.15; H, 7.91; S, 35.96. Found: C, 47.08; H, 7.94; S, 35.82.

Similar results (yield, stereoselectivity) were obtained when the oxidation was carried out with sodium metaperiodate or with hydrogen peroxide.

Oxidation of 1,3-dithiolane 1-oxide (**11**) *with sodium metaperiodate.* A solution of 2.25 g (10.5 mmol) of sodium metaperiodate in 25 ml of water was added dropwise to a stirred solution of **11** (1.22 g., 10.0 mmol) in 90 ml of methanol at −10 to −3°C. After 20 min, the mixture was allowed to warm to room temperature and stirred for 18 hr. The solvents were removed in vacuo, and the residue was extracted with two 100-ml portions of chloroform and 100 ml of ethanol. Evaporation of solvents gave 1.307 g (95%) of 1,3-dithiolane *trans*-1,3-dioxide (**18**) which was homogeneous to TLC. Two recrystallizations from ethanol afforded the analytical sample: mp 155.5–156.5°C reported[5]; mp 157–158.5°C); IR(KBr) 1015 cm^{-1} (br, S = O), NMR ($CHCl_3$) δ 3.67 (m, 8 lines, 4, $-CH_2CH_2-$) and 4.11 ppm (s, 2, C-2 H); mass spectrum *m/e* (rel intensity) 138 (34), 110 (20), 108 (16), 46 (100).

Anal. Calcd. for $C_3H_6O_2S_2$: C, 26.07; H, 4.38; S, 46.40. Found C, 26.12; H, 4.40; S, 46.24.

Oxidation of 1,3-dithiolane (**10**) *with two equivalents of m-chloroperoxybenzoic acid.* *m*-Chloroperoxybenzoic acid (11.04 g, 54.4 mmol) in 200 ml of dichloromethane was added dropwise to a solution of **10** (2.89 g, 27.2 mmol) in 100 ml of dichloromethane over a 2 hr period at −30 to −35°C. After storage at −25°C overnight, the precipitated *m*-chlorobenzoic acid was removed by filtration, and the solvent was removed from the filtrate in vacuo. The solid white residue was extracted with 150 ml of ether, leaving 3.50 g (93.2%) of product, mp 138–141°C. Analytical TLC (silica gel; 10% methanol/chloroform) showed only one spot. The NMR spectrum was identical to that of **18**. Recrystallization of the crude product from 2-propanol gave 3.10 g (83%) of **18**, mp 148–149°C.

Oxidation of cis-2-phenyl-1,3-dithiolane 1-oxide (**9**). According to the usual procedure, 142.3 mg of **9** was treated with *m*-chloroperoxybenzoic acid to yield 139 mg (90%) of **12** 169.5–170.5°C. Recrystallization from ethanol gave the analytical sample: mp 178–178.5°C; ir (KBr) 3060, 3030, 2980, 2930, 2885, 1500, 1450, 1400, 1040 (s), 1025 (vs), 1095, 770, and 695 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.85 (m, 4, $-CH_2CH_2-$), 4.87 (s, 1, C-2 H), and 7.0–7.5 mmp (m, 5, Ph); mass spectrum *m/e* (rel intensity)

214 (0), 198 (12), 137 (43), 122 (78), 121 (93), 108 (100), 105 (56), 77 (48), 60 (62).

Anal. Calcd. for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70; S, 29.93. Found: C, 50.25; H, 4.75; S, 30.03.

Oxidation of trans-2-phenyl-1,3-dithiolane 1-oxide (**8**). Oxidation of **8** (430 mg, 2.17 mmol) with MCPBA resulted in 431.4 mg (93.2%) of crude product, mp 123.5–130.5°C. The NMR spectrum of this material showed *ca.* 74% **13** and 26% **12**. The crude product was chromatographed on three silica gel plates, using 20% 2-propanol/carbon tetrachloride as developing solvent. Extraction of the lower R_f band gave 294.4 mg (63%) of 13 mp 160–161°C (dec.); extraction of the higher R_f band gave 63.8 mg (14%) of 12, mp 168–170°C (dec). Recrystallization of crude **13** from ethanol afforded the analytical sample: mp 187.5–188.5°C; ir (KBr) 3085, 3060, 3025, 2990, 2975, 2930, 2879, 1490, 1445, 1390, 1105, 1040 (vs), 1025 (vs), 1000, 765, and 690 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.4–3.9 (m, 4, $-CH_2CH_2-$), 4.99 (s, 1, C-2 H), and 7.0–8.1 ppm (m, 5, Ph); mass spectrum *m/e* (rel intensity) 214 (1), 198 (2), 137 (34), 122 (53), 121 (70), 110 (31), 108 (100), 105 (36), 60 (36).

Anal. Calcd. for $C_9H_{10}O_2S_2$: C, 50.44, H, 4.70; S, 29.92. Found: C, 50.33; H, 4.71; S, 29.84.

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