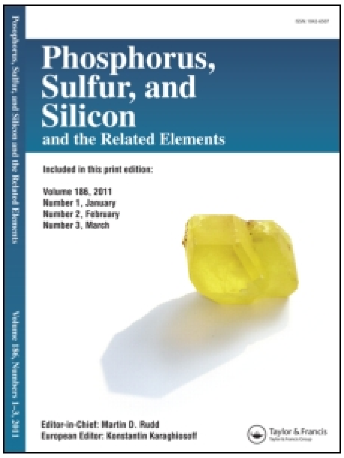

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REARRANGEMENT MECHANISMS OF SOME CYCLIC SULFOXIDES

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REARRANGEMENT MECHANISMS OF SOME CYCLIC SULFOXIDES.

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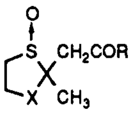
Abstract : Under neutral conditions cis sulfoxides **5** underwent a sigmatropic rearrangement with 2-methylene hydrogens to give sulfenic acids **18**, followed by cyclization to dihydro-1,4-dithiins **2**. The trans sulfoxides **6** rearranged involving 2-methyl hydrogens to form isomeric dihydrodithiins **3** via sulfenic acids **19**. In the reactions of both the sulfoxides, sulfides **4** and disulfides **11** were also formed as minor side products. In the presence of acid catalyst cis sulfoxides **5** produced **2** in quantitative yields while the trans sulfoxides **6** gave a mixture of **2** and **3**. The mechanism of formation of **2**, **3**, **4** and **11** are discribed.

The ring expansion reaction of appropriately substituted 1,3-dithiolane, 1,3-oxathiolane and 1,3-thiazolidine sulfoxides 1 is of considerable mechanistic interest as well as synthetic utility. We have previously reported the rearrangement of 1,3-oxathiolane sulfoxides[1] and 1,3-thiazolidine sulfoxides[2]. This paper presents rearrangement of 1,3-dithiolane sulfoxides 1 (X = S) and compare this with those of two previous series.



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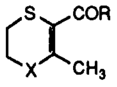

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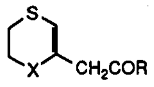
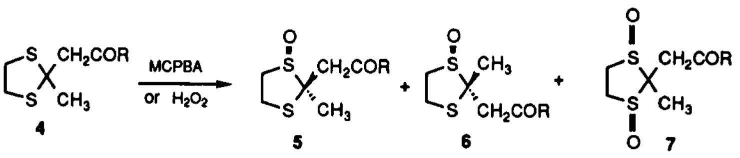


3

R = a NHC_6H_5 ; b OCH_3
X = S, O, NAc

As shown in Scheme I oxidation of the sulfide **4** gave a mixture of cis and trans monosulfoxides **5** and **6** as major and minor products, respectively, plus a small amount of disulfoxides **7**. The structural assignments of cis and trans sulfoxides 5 and 6 were based on ^1H NMR spectroscopy and the regiospecific deuteration of the two isomers giving products **19** and **21** corresponding to **5** and **6**, respectively (Scheme II)[3]. The results of deuteration provide evidence for a sulfoxide-sulfenic acid equilibrium[4] and show that no isomerization occurs to interconvert cis and trans sulfoxides 5 and 6. That the thermal reactions of the sulfoxides are sigmatropic was substantiated by determing the kinetic deuterium isotope effect for **5a/22a** and **6a/23a**, and the k_H/k_D was

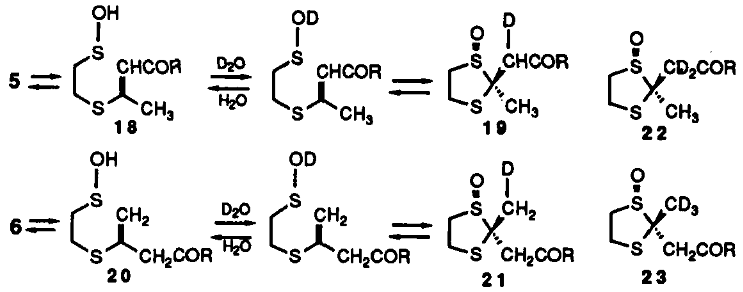
Scheme I



R = a NHC_6H_5 ; b OCH_3 ; c OH

found to be 2.52 and 5.23, respectively, which are in the range of expected values for the primary isotope effect in β-cis elimination[5].

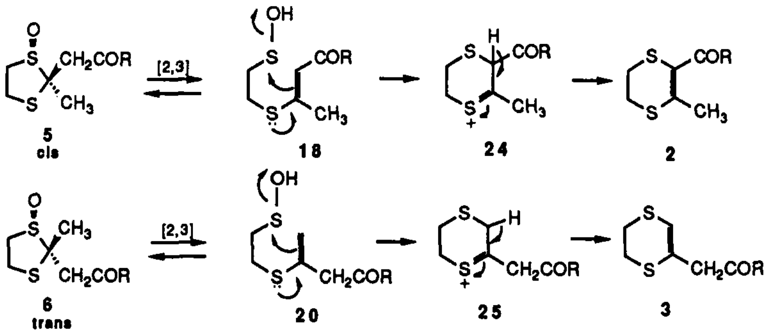
Scheme II



R = a NHC_6H_5 ; b OCH_3

Under neutral conditions thermal reactions of cis and trans sulfoxides **5** and **6** in toluene or C_6H_6-DMF at reflux produced expected dihydrodithiins **2** and **3**, respectively, in good yields plus sulfides **4** and disfilides **11** as side products. The structures of **2**, **3** and **11** were identified by elemental and spectral analyses. The mechanism of ring expansion reactions is shown in Scheme III.

Scheme III

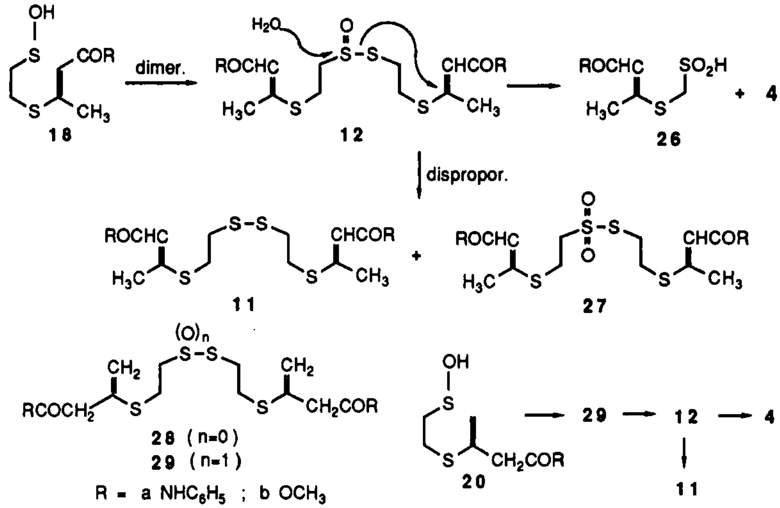


R = a NHC_6H_5 ; b OCH_3

Based on the results of foregoing deuteration reactions the reaction of cis sulfoxides **5** proceds via sulfenic acid **18** as generated by a sigmatropic rearrangement with 2-methylene group, followed by cyclization to the sulfonium ions or carbocations **24** which lose the acidic proton to produce dihydrodithiins **2**. Likewise, in the rearrangement of trans sulfoxides[6] a sigmatropic ring opening may occur involving 2-methyl group to form sulfenic acids **20** which cyclize to sulfonium ions **25** to give the expected isomeric dihydrodithiins **3**. The formation of by-products **4** and **11** is mechanistically intriguing. The probable origins of these are shown in Scheme IV[6].

In the presence of PTSA as catalyst the cis sulfoxides **5** in refluxing benzene produced dihydrodithiins **2** in quantitative yield. On the other hand the trans isomers under the same conditions gave a mixture of normal dihydrodithiins **2** and isomeric dihydrodithiins **3**.

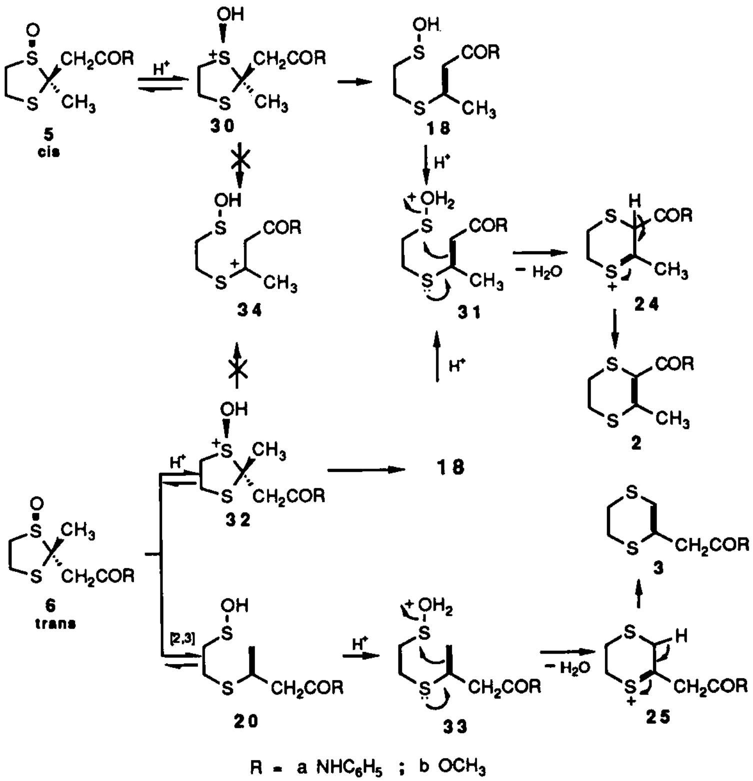
Scheme IV



R = a NHC_6H_5 ; b OCH_3

In Scheme V an overall mechanism is summarized. The ring opening of the cis

Scheme V



R = a NHC_6H_5 ; b OCH_3

sulfoxides occurs via protonated sulfoxides **30** to give sulfenic acid **18** by a concerted β-elimination rather than by a stepwise mechanism involving carbocations **34**.

The sulfenic acids **18** thus formed is protonated, followed by cyclization to sulfonium ion **24** to give dihydrodithiins **2**. The reaction of the trans sulfoxides **6** is quite interesting. The ring opening occurs involving two competitive mechanistic pathways. Namely, one proceeds via protonated sulfoxides **32** to give sulfenic acid **18** by concerted β-elimination involving only active methylene hydrogens to give the same sulfenic acid **18** as the cis isomers, producing the normal dihydrodithiins **2**. The other one preoceeds via sigmatropic rearrangement to give sulfenic acid **20** which, by acid catalyzed dehydration, produces isomeric dihydrodithiins **3** via **25**. Supporting evidence for these two reaction pathways comes from the observed variation in the product ratio **2/3** with the amount of acid used, that is, the product **2** increases with the amount of PTSA in inverse propotion to **3**. Thus, at higher acid catalyst concentration the chance for **6** to react by sigmatropic ring opening with 2-methyl group to give **20** is decreased as compared to acid catalysed ring opening to give **18**. It was found that isomerization of **6** to **5** did not occur during the acid catalysed reaction. Interestingly, the lack of isomerization can be evidence for a concerted β-elimination of these protonated sulfoxides **30** or **32** to produce a common sulfenic acid **18** without involvement of the carbocation **34**. If **34** were formed, it should undergo nonstereospecific recyclization to give a mixture of the cis and trans isomers[2].

By contrast, in the 1,3-oxathiolane sulfoxides (X=O)[1,7] and 1,3-thiazolidine sulfoxides (X=NAc)[2] isomerization occurs to interconvert cis and trans sulfoxides in the presence of acid catalyst, suggesting that carbocations analogous to **34** were formed, probably due to greater effect of nitrogen or oxygen atom on stabilizing carbocation as compared with sulfur atom.

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