THE REACTION OF ω-VINYL PRIMARY DISULFIDE WITH HALOGEN

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Several olefinic disulfides were prepared by ordinary methods and allowed to react with halogenating reagents. The products obtained in this reaction were two types of β-halothiacycloalkanes as one would expect, ie., α-halomethylthiacycloalkane and β-halothiacycloalkane, which are not readily prepared by usual procedures.

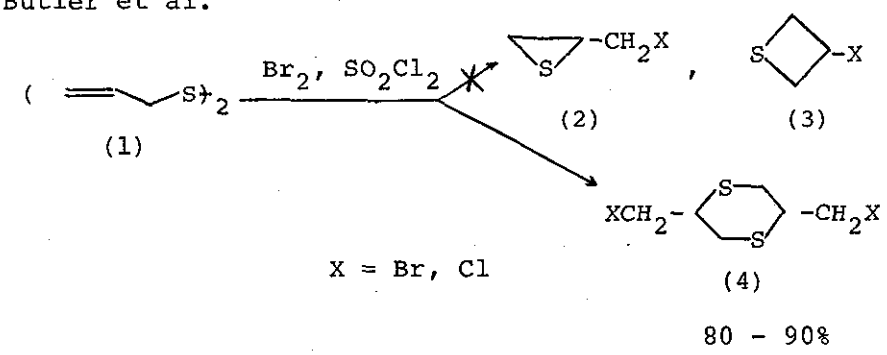
The trans-annular addition of sulfur dichloride to cyclic diolefins, gives sulfur bridged β,β´-dichlorothiacyclic compounds in fairly good yields.[1] These authors suggested that the reaction intermediate is a cyclic alkenesulfenyl chloride, formed by the addition of sulfur dichloride to one part of double bond of the cyclic diolefin. A similar suggestion was also made by Paquette et al.[2], concerning the stereochemistry of the halogenation of (3,3,1)-thiacyclononane.

We have studied the reaction of olefinic disulfide with halogenating reagents, such as, Cl_2, Br_2, I_2, and SO_2Cl_2, hoping to obtain similar results via the initial formation of alkenesulfenyl halides and also to make clear the behavior of alkenesulfenyl halide by comparing the results with those of the cyclization reaction of $CH_2=CH(CH_2)_n-X$ (X: leaving group) in the solvolysis.[3] All alkenyl disulfides were treated with halo-

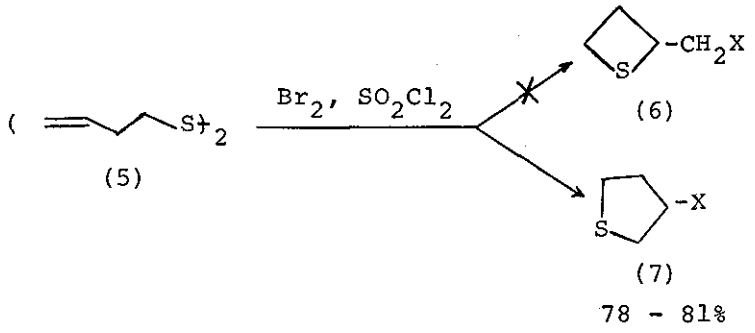
genating reagents in dichloromethane at dry-ice temperature.

The conversion(%) was determined by weighing the distillable products, which were also analyzed by glc to estimate the product ratio.

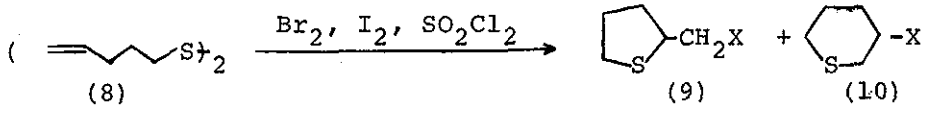
In the reaction of allyl disulfide(1), the expected cyclized products, such as, 3-chloropropylene episulfide(2) and 3-chlorothietane(3), were not formed but 2,5-dichloromethyl-1,4-dithiane(4) was obtained, as was already reported in the similar reaction by Butler et al.[4)]



In this case the bicyclic episulfonium intermediate(12) in Scheme I, is so highly strained, and unstable that it would eventually dimerize readily to form (4). In the case of 3-butenyl disulfide(5): bp 75-75.5°/3mmHg, Elemental Anal., Calcd., C%; 55.12, H%; 8.10, Found, C%; 54.80, H%; 8.43, a less strained 5-membered cyclic product, 3-halothiacyclopentane(7): (7a, (X=Cl)) : bp 89-90°/40mmHg, which shows an identical pattern of ir and nmr spectra to those of the authentic sample obtained by chlorination of 3-hydroxythiacyclopentane, was formed, however, no 2-halomethylthiacyclobutane(6), a more strained 4-membered compound, was found to be formed.



When the methylene chain is lengthened to 3; 4-pentenyl disulfide(8): bp 95-6°/2mmHg, Elemental Anal., Calcd., C% 59.35, H%; 8.97, Found, C% 58.97, H%; 9.26, the products obtained were mixture of 2-halomethylthiacyclopentane(9) and 3-halothiacyclohexane(10): (10a, (X=Cl)): bp 88-89°/33mmHg, (10b, (X=Br)): bp 97-98°/15mmHg, (10c, (X=I)): bp 75-76°/2mmHg, which show identical patterns of ir and nmr spectra to those of the authentic samples prepared from 3-hydroxythiacyclohexane. Compound(9) is less stable than compound(10) and isomerizes readily to compound(10) at room temperature eventually forming the thermodynamically equilibrated mixture.[5] In this case the initial product ratio was determined by the ratio of the stable sulfone derivatives, which were prepared by the direct oxidation of the cold reaction mixture of the uneqilibrated β-chlorosulfides with m-chloroperbenzoic acid.

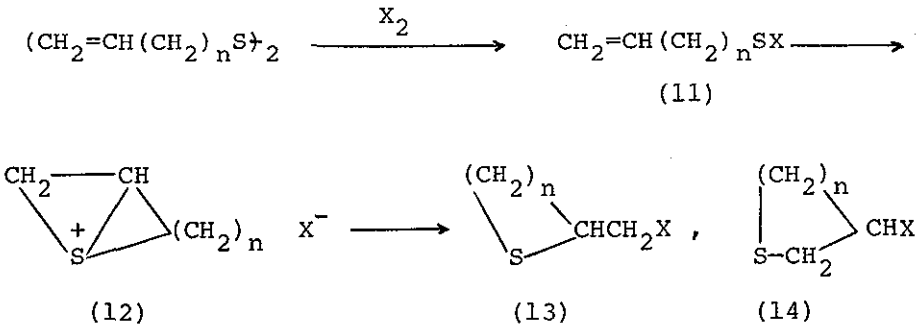


X=Cl	75.3%	24.7%
X=Br	81.4%	18.6%

These results indicate that although there are two reacting

sites of halogen, ie., the double bond and the S-S group, the attack of the halogen on the S-S linkage takes place more readily than the addition to the double bond under such a condition in view of the lack of the dihalo-addition product.

Therefore, β-halothiacycloalkanes are considered to be formed by the intramolecular cyclization of the alkenesulfenyl halide initially formed via the formation of the episulfonium ion (12) A certain episulfonium ion was actually isolated in a fairly stable form.[6)]



Scheme I

In all cases except allyl disulfide(1), the products are either α-halomethylthiacycloalkanes(Anti-Markovnikov type addition compound(13)) or β-halothiacycloalkanes (Markovnikov type addition compound(14)) or both. In the case of allyl disulfide(1) the product(4) is also anti-Markovnikov type addition compound. Inspection of product-distributions suggests that the stability of the products plays the most important role in determining which products are formed preferentially.

Since the intermolecular cyclization of alkenesulfenyl halide,

presumed to be the intermediate initially formed, is considered to proceed via the concerted participation of the terminal double bond in the S-X bond cleavage, it is interesting to compare these data with those of the similar intermolecular cyclization reactions of $CH_2=CH(CH_2)_nX$ (X=leaving group) in the solvolytic reaction. Trahanovsky et al. have reported earlier that the cyclization occurred in the trifluoroethanolysis of ω-vinyl nosylates in a fair yield.[3] In this case, however, the formation of a large ring compound is favored over that of smaller one because of the higher stability of the secondary carbonium ion than that of the primary one. On the other hand the prefered product in the halogenative cyclization of 4-pentenyl disulfide(8) is the smaller ring compound. Thus, the result is similar to the intermolecular addition reaction of the sulfenyl halide to olefin in which the anti-Markovnikov type addition is predominant.[7] The plausible explanation for the anti-Marko nikov type orientation of the addition is that the reaction is controlled by the steric stabilization of the product formed by the subsequent ring opening of the episulfonium intermediate(12) by the attack of halide ion at either one of the two attacking sites of episulfonium ring.

References;

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