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Pyrolysis of 1,2-Epithiocyclohexane

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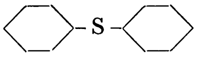
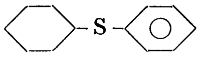
Synopsis. Dicyclohexyl sulfide, cyclohexyl phenyl sulfide, dicyclohexyl disulfide, 2,3,5,6-bis(tetramethylene)-1,4-dithiane, cyclohexanethiol and cyclohexyl cyclohexenyl sulfide were obtained by the pyrolysis of 1,2-epithiocyclohexane apparently *via* the attack of sulfur radical species, formed by the pyrolysis of 1,2-epithiocyclohexane, on the double bond of cyclohexene.

Certain thiiranes are known to split off sulfur upon pyrolysis to give the corresponding olefins.[1] A recent report indicates that sulfur-containing products are formed by the pyrolysis of thiiranes.[2] Nevertheless, little is known about the reaction of olefins with sulfur extruded from thiiranes.[1,3]

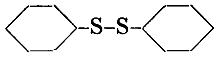
We have carried out the liquid phase pyrolysis of 1,2-epithiocyclohexane and examined products formed in this reaction in the hope of sheding light on the reaction of cyclohexene with sulfur species[4] which would be formed by the pyrolysis of 1,2-epithiocyclohexane. The pyrolyzed products were found to consist of six gas-chromatographically separable components (A,B,C,D, E,F). From mass and NMR spectroscopic data and by comparison with authentically synthesized samples, the pyrolyzed products were identified as dicyclohexyl sulfide (A), cyclohexyl phenyl sulfide (B), dicyclohexyl disulfide (C), 2,3,5,6-bis(tetramethylene)-1,4-dithiane (D), cyclohexanethiol (E) and cyclohexyl cyclohexenyl sulfide (F).



(A)



(B)



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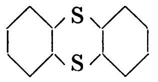
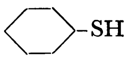
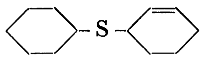


(D)

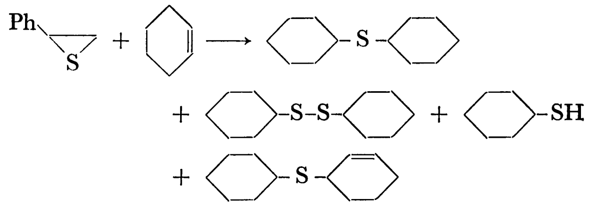


(E)

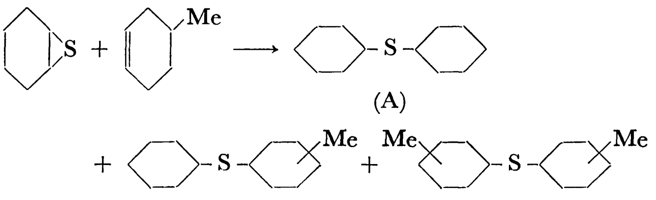


(F)

A small amount of benzene was formed apparently by the hydrogen abstraction of cyclohexene with the sulfur species formed initially.[5] The formation of hydrogen sulfide was also observed but none of elemental sulfur. When 1,2-epithiocyclohexane was heated at 210 °C for one hour in a sealed tube, compounds A,B,C,D and E were formed in 22, 4, 12, 1, and 6% yields respectively. Compound F was formed only at an early stage of the reaction but might give a compound such as B after abstraction of allylic hydrogens of F by the sulfur species. Actually, B is formed upon heating F with elemental sulfur. However, it cannot be formed by the reaction of the episulfide with benzene which is formed by the hydrogen abstraction of cyclohexene, since compound B was not formed upon heating 1,2-epithiocyclohexane in benzene. When a mixture of 1,2-epithiocyclohexane and ten equimolar amount of cyclohexene was heated at 210 °C for one hour in a sealed tube, the yield of A increased while F was also formed. This suggests that the hydrogen abstraction from F by the sulfur species is depressed by excess cyclohexene. In this case, the yields of A,C,E, and F based on the amount of episulfide used, were found to be respectively 63, 2, 2, and 7%. When a mixture of excess cyclohexene and stilbene episulfide was heated under the same conditions, compounds A,C,E, and F were similarly formed, their yields being respectively 57, 1, 2, and 8%. When a similar mixture of cyclohexene and styrene episulfide was heated, compounds A,E, and F were formed in respective yields of 26, 1, and 5%. A similar result was obtained upon heating a mixture of excess cyclohexene and 1,2-butene episulfide. These experiments suggest that a sulfur radical species produced by the pyrolysis of a certain episulfide attacks the double bond of cyclohexene as in the pyrolysis of 1,2-epithiocyclohexane.



An interesting problem in the pyrolysis of episulfide is whether the two carbon–sulfur bonds of episulfide are cleaved simultaneously or consecutively, eventually yielding the corresponding olefin and sulfur. In order to clarify the mode of the C–S bond cleavage, we carried out the following experiments. An equimolar mixture of cyclohexene and 4-methylcyclohexene containing the same amount of styrene episulfide was heated in a sealed tube. Dicyclohexyl sulfide (A), cyclohexyl methylcyclohexyl sulfide (1A) and dimethyldicyclohexyl sulfide (2A) were formed in the molar ratio 1: 2: 1. This is the statistical ratio, since the sulfur species, formed by the pyrolysis of the styrene episulfide, will attack cyclohexene and 4-methylcyclohexene with equal ease and hence the amount of 4-methylcyclohexyl cyclohexyl sulfide formed will be twice that of dicyclohexyl or di-4-methylcyclohexyl sulfide in this reaction. The products containing one methyl group, *viz.* 3-methylcyclohexyl and 4-methylcyclohexyl sulfides, were formed nearly in the same yields. When an equimolar mixture of 1,2-epithiocyclohexane and 4-methylcyclohexene was heated in a sealed tube, compounds A, 1A, 2A, were formed in the molar ratio 1: 2.3: 1.2. This is similar to the results in the former case, suggesting that the sulfur species is formed by the pyrolysis of 1,2-epithiocyclohexane and attacks both the cyclohexene formed by the pyrolysis and 4-methylcyclohexene with equal ease; thus, 1,2-epithiocyclohexane seems to give sulfur and cyclohexene upon pyrolysis and not the stable thiyl radical. When 1,2-epithiocyclohexane and 4-methylcyclohexene were heated in the molar ratio a: b, the ratio of products A, 1A, and 2A was found to be represented approximately by $a^2: 2ab: b^2$. However, the formation of compound A is usually slightly smaller than the calculated amount. This is because 4-methylcyclohexene, being present in the system form the beginning, will have a slightly greater chance of being attacked than cyclohexene on account of the small amount of cyclohexene formed in the early stage of the reaction.



(A)

(1A)

(2A)

There is a possibility that compounds 1A and 2A are formed in the reaction of 4-methylcyclohexene with some other reaction products. A small amount of 1A was formed upon heating a mixture of cyclohexanethiol and 4-methylcyclohexene, but neither A nor 2A was formed. When a mixture of A and 4-methylcyclohexene was heated, 1A and 2A were obtained besides unreacted A, but the molar ratio of compounds A, 1A, and 2A was found to be 100: 9: 2. Compound 2A was not obtained in a large amount. In another experiment, a mixture of compound C and 4-methylcyclohexene was heated but no sulfide was formed. Futhermore, when an equimolar mixture of 1,2-epithiocyclohexane and 4-methylcyclohexene was heated for 4 min, the initial reaction products A, 1A, and 2A were formed in the molar ratio 1: 10: 17. Thus, 2A was formed in a large amount in the early stage of the reaction, This suggests that the sulfur species released from 1,2-epithiocyclohexane mainly attacks 4-methylcyclohexene, since there is little cyclohexene formed in the early stage of the pyrolysis. Thus it is clear that 1A and 2A are formed in the early stage of the reaction and other products such as the thiol, sulfide and disulfide which are formed in the course of the reaction would rarely undergo decomposition and recombination with 4-methylcyclohexene; therefore, the molar ratio of the products A, 1A, and 2A, 1: 2: 1, does not result from the reaction of cyclohexene and 4-methylcyclohexene with other products but from the reaction with the sulfur species. From an overall picture of the whole process, these experimental results suggest that at the relatively high temperature we employed (210 °C) the two carbon–sulfur bonds of 1,2-epithiocyclohexane may be cleaved simultaneously, resulting in the formation of cyclohexene and sulfur species. If only one of two carbon–sulfur bonds of 1,2-epithiocyclohexane were cleaved to form a highly stable biradical intermediate, compounds A and 2A would not be formed in this reaction.

Experimental

Materials. 1,2-epithiocyclohexane, styrene episulfide and 1,2-butene episulfide were prepared from the corresponding epoxy compounds with potassium thiocyanate.[6] Stilbene episulfide was obtained by reacting stilbene oxide with thiourea.[7] Dicyclohexyl sulfide, cyclohexyl phenyl sulfide and cyclohexyl cyclohexenyl sulfide were synthesized by the reaction of the corresponding bromide with the thiol in the usual way. Dicyclohexyl disulfide and cyclohexylcyclohexenyl disulfide were synthesized by heating the corresponding chloride with sodium disulfide.[8] 4-methylcyclohexyl cyclohexyl and 3-methylcyclohexyl cyclohexyl sulfides were prepared by treating 4-methylcyclohexyl and 3-methylcyclohexyl bromides with cyclohexanethiol.

Reactions. A typical run was carried out as follows. 1,2-epithiocyclohexane (0.3 g) or a mixture of 1,2-epithiocyclohexane and cyclohexene was heated at 210 °C for one hour in a vacuum sealed tube. After completion of the reaction, evolved gas was admitted into a solution of cupric sulfide and hydrogen sulfide was identified by trapping it as cupric sulfide. The liquid products of the reaction mixture were analyzed by vpc, NMR and mass spectroscopies. Their mass spectra indicate that the cracking patterns of the six compounds are similar and all of them have the cyclohexyl ring. Their parent peaks are given at *m/e* 198, 196, 192, 230, 228, 116. Since both 2,3,5,6-bis(tetramethylene)-1,4-dithiane and cyclohexyl cyclohexenyl disulfide should give the same parent peak of 228, cyclohexylcyclohexenyl disulfide was synthesized independently but was not found to be the reaction product by vpc. Compounds A, C, and E were obtained in sufficient amounts to enable their identification by NMR spectroscopy. The NMR spectrum of A gave a broad singlet at τ-value of 7.2 and a multiplet centered on a τ-value of 9.4. C and E gave similar spectra.

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