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SYNTHESES AND REACTIVITIES OF SULFUR-CONTAINING HETEROCYCLES

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The rapid and stereospecific trans additions of sulfenyl halides to olefins provide possibility for the synthesis of S-containing heterocycles when the reactions are carried out intramolecularly. The symmetric disulfides of 4-pentenyl (1), 4-methyl-4-pentenyl (2), trans-4-hexenyl (3), cis-4-hexenyl (4), 5-methyl-4-hexenyl (5), 2-propenyl (6), 3-butenyl (7), 3-cyclopentenylmethyl (8), 3-methyl-3-cyclopentenylmethyl (9), 3-cyclohexenylmethyl (10), 2-cyclopentenylmethyl (11), and 3-cyclohexenyl (12) were prepared and reactions with chlorine were examined. All reactions proceeded smoothly even at -30∼-50° and gave the corresponding β-chloro sulfides quantitatively. Although the orientation of ring closure depends upon the structure of olefin, the state of substitution, ring-size formed by the ring closure, and so on, the ratios of two isomers produced initially, because of their outstanding reactivities, trended usually to the high ratios of a more stable isomer depending upon the thermal stabilities.

The disulfides (1, 2) gave initially the corresponding 5-membered rings (79.6%, 95.4%) as a major isomer, which, in thermal equilibration, changed to 6-membered rings (81.9%, 95.6%). 3, 4, and 5 yielded 6-membered rings (78%, 100%, 100%) initially and they changed to 75%, 56.8%, and 35.8% respectively after isomerization. The cyclization from 8 and 9 gave 6-exo-chloro-2-thianorbornane and its 1-methyl derivative as a single product in quantitative yields. 4-exo-Chloro-6-thiabicyclo[3.2.1]octane was obtained as a sole product from 10 after the rapid equilibration of an initial mixture. Systems (6, 7, 11, 12) which involve a mechanistically unfavored intermediate (thietanium ion) did not result in simple ring closure under the same condition. The reaction with bromine in a diluted solution (final concentration; 10^{-2} mole/ l), however, gave an expected product in a moderate yield.

Structural characterization of all products was done by spectroscopic technique (pmr, mass). It is considered that β-chloro sulfides as a result of cyclization would be useful for stereochemical studies in sulfur chemistry and as synthetic intermediates to the various derivatives of S-containing heterocycles.