THE ROLES OF HETEROATOMS IN EPOXIDE OPENING

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In connection with our studies on the roles of heteroatoms (N,S,O) in solvolytic reactions, the effects of the heteroatoms in ring opening of epoxides, 3-methylene epoxides of tetrahydropyran (1), tetrahydrothiopyran (2), and N-methylpiperidine (3) and *cis-trans* stereoisomers of 2-*t*-butyl-5-methylene-1,3-dithiane epoxides (4,5), were examined. All epoxides were synthesized according to Corey's procedure from the corresponding cyclanones. The epoxide opening reactions carried out for 1~3 are the following (the reaction d for 4 and 5); (a) reduction with lithium aluminum hydride, (b) reduction with lithium metal in ethylenediamine, (c) reduction with lithium borohydride-borane, (d) acid-catalyzed opening with acetic acid, and (e) acidic catalysis with aq. hydrochloric acid.

No appreciable effects of heteroatoms were observed in the reactions a and b for 1 and 3. The reactions c and d for 2 resulted in the predominant formation of the rearranged 5-membered derivatives. The compounds 4 and 5 reacted readily with acetic acid and yielded quantitatively the corresponding 5-membered alcohol-acetates with retention of configuration. These results strongly suggest that an enormous amount of participation, particularly by the sulfur atom, is also involved in the opening reaction of epoxides as well as that observed in solvolysis.