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THE EFFECT OF α-EPOXY AND EPISULFIDE GROUPS IN THE SOLVOLYTIC REACTION(1)

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The unusally high rates of solvolysis of cyclopropylcarbinyl derivatives have recieved considerable attentions in recent years and the interesting but still controversial carbon-carbon σ-bond participation has been proposed to explain the markedly large reactivity(2).

Epichlorohydrin which has a similar strained structure and is capable of both oxygen-carbon σ-bond participation and classical electron pair participation is anticipated to have been higher reactivity in solvolysis, however, has received scant attention. We wish to report the unusually high reactivities of both epichlorohydrin(3-chloropropylene oxide) and 3-chloropropyllen sulfide. They are considerably more reactive than cyclopropylcarbinyl chloride as shown in Table I.

TABLE I

First-Order Rate Constants in the Acetolysis at 105°C

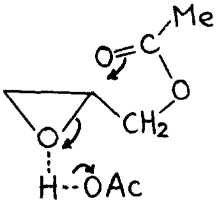
Compounds	k_1 (sec^{-1})	Rel. rate
Allyl chloride	$\sim 4 \times 10^{-7}$	1
Cyclopropylcarbinyl chloride	1.21×10^{-5}	30
3-Chloropropylene oxide	5.93×10^{-5}	~100
3-Chloropropylene sulfide	1.22×10^{-3}	3,000

The kinetic rates of the acetolysis reactions of these compounds in glacial acetic acid were measured by following the gradual loss of the original compounds by GLC, because the formation of chloro-compound among the products dose not encourage the use of the Vorhart method to follow the formation of chloride ion. While, fairly good first order rate constants are obtained within the experimental error of less than 5%, 90% of the products of the acetolysis of 3-chloropropylene oxide after 3 hours of heating at 105°C were characterized by IR, NMR and elemental analyses and the results are shown in Table II. Though, the analysis of the products from 3-chloropropylene sulfide is not as complete as that of the oxygen analogue, the pattern of the distribution of products appears to be similar and the formation of the 4-membered 3-acetoxy thietane was also observed. The formation of these 4-membered heterocyclic compound, ie., 3-acetoxy oxetane and its sulfur analogue, suggests that the nucleophilic participation of both oxygen and sulfur atoms are involved in the reaction. The complete lack of 3-acetoxypropylene oxide in the reaction of 3-chloropropylene oxide is interesting but can be rationalized on the basis of the participation of carbonyl group(3) of 3-acetoxypropylene oxide, either forming 5- or 6-membered cyclic transition state. In fact, this compound reacts very rapidly with acetic acid with the rate constant of 2×10^{-3} sec^{-1}.

TABLE II

Products of the Reaction of 3-Chloropropylene Oxide with Acetic Acid

Compounds	Yield (%)
3-Acetoxypropylene oxide	0
3-Acetoxy oxetane	11.2
1,3-Dichloro-2-propanol	27.4
1-Chloro-3-acetoxy-2-propanol	24.8
3-Chloro-2-acetoxy propanol	19.0
1,3-Diacetoxy-2-propanol	7.8
Not identified product	~0



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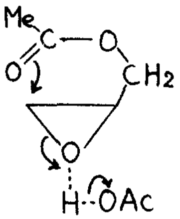
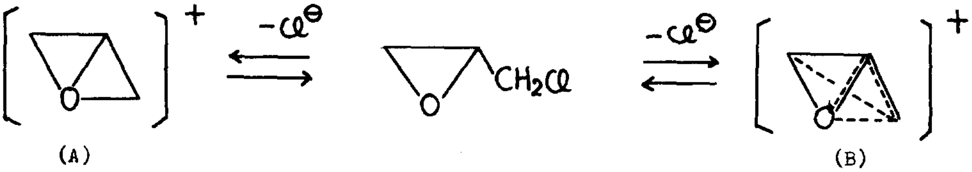


A question remains as to the nature of the transition state of the solvolysis of the epoxy compound. The classical electron-pair participation may lead to the bridged carbonium ion(A) which in turn may lead to a variety of products. The non-classical oxygen-carbon σ-bond participation may lead to another bridged carbonium ion(B), which is also capable of affording the same products. At present, there are scant concrete supporting data available to make a choice between the two. However, the lack of the electron pair participation in the solvolysis of 2-haloethyl ether(4) and the unusually large enhancement of the rate in this epoxide seems to favor the non-classical participation in the transition state of the acetolysis.



A similar argument may be developed for the acetolysis of the episulfide. However, since the size of the anchimeric assistance does not seem to exceed so markedly that of the 2-sulfide group in the solvolysis of 2-chloroethyl alkyl sulfide(4) (Calc. $\sim 10^{-4}$sec^{-1}), the classical electron-pair participation may be able to explain satisfactorily both the rate enhancement and the product distribution of the reaction of the episulfide. In order to shed further light on the mechanistic schemes, a tracer work is desirable and now underway here.

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