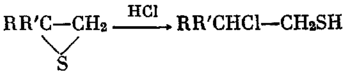
OPENING OF THIIRANE RING BY HYDROGEN HALIDES

A. V. Fokin, A. F. Kolomiets,
and T. I. Fedyushina

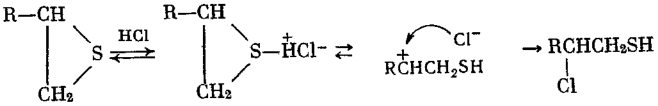
UDC 541.124:542.92:547.71:546.121

Based on the data given in [1-5], epithio compounds react unambiguously with hydrogen halides, in which connection the thiirane ring is cleaved at the least hydrogenated carbon atom, i.e., contrary to the Krasuskii rule.



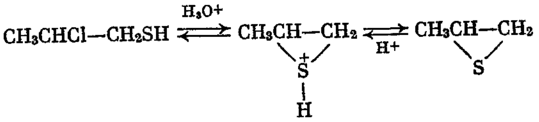
Later [6, 7], employing GLC and NMR, it was shown that the propylene, isobutylene, and chloropropylene sulfides [6], and α,β-epithioglycidic acids [7] are cleaved by hydrogen chloride to give a mixture of products with a "normal" and "abnormal" structure. The "normal" cleavage of the C–S bond at the most hydrogenated C atom prevails (66-96%). The secondary or tertiary thiols that are formed here tend to isomerize under the reaction conditions to the primary thiols, which explains to a certain degree the reasons for the opposite results given in [1-5] and [6, 7].

The reactions of anhydrous HCl and HBr with thiiranes are second order [8]. In the opinion of the authors, this testifies to the formation of carbonium cations during reaction. Similar theories were also expressed earlier [2]



The possibility of similar reactions proceeding by the carbonium mechanism via the step of forming episulfonium cations is also discussed in [6].

The concept that the carbonium mechanism holds for the opening of the thiirane ring by hydrogen halides contradicts certain experimental data. Thus, cyclohexene sulfide stereospecifically undergoes trans-cleavage by HCl [9]. Ethylene sulfide is polymerized in dilute HCl solution [10, 11], where the formation of the carbonium cation is most probable in view of the efficient solvation of the chlorine anion. Substituted thiiranes are formed under these conditions, apparently via the step of the episulfonium cation [6, 7]



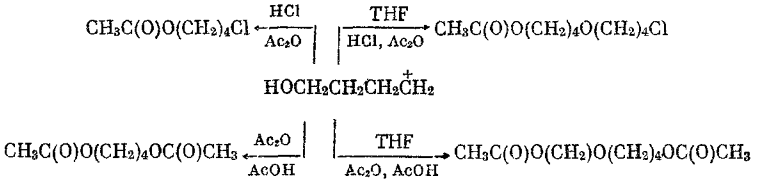
Sulfuric acid, which cleaves three-membered heterocycles to carbonium cations, initiates the polymerization of epithioalkanes [10, 11].

We studied the transformations of ethylene sulfide when it is reacted with HCl in the presence of acid anhydrides. For comparison we used THF in similar reactions, the cleavage of which by the carbonium mechanism is considered to be the most probable. It was shown that the reactions of THF with HCl in Ac_2O, or in a mixture of Ac_2O and AcOH, is always accompanied by the insertion of the acetoxy group. From THF and HCl under these conditions we obtained and identified 4-chlorobutyl acetate, 1,4-diacetoxybutane, and the 4-chloro-4'-acetoxy- and 4,4'-diacetoxydibutyl ethers. Similar results were also obtained

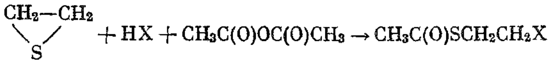
---

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 670-673, March, 1975. Original article submitted July 10, 1974.

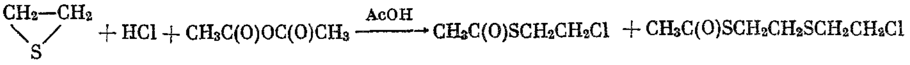
in the reactions with HBr. The ratio of the formed products depends on the order of mixing the reactants. When THF is added to a saturated solution of HCl in Ac_2O the main product is 4-chlorobutyl acetate. The slow addition of HCl to a mixture of THF, Ac_2O, and AcOH leads mainly to 1,4-diacetoxybutane. This character of the process testifies to the carbonium mechanism of cleaving the furanidine ring by hydrogen halides



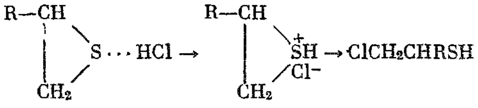
Entirely different results are obtained when ethylene sulfide is reacted with hydrogen halides in the presence of Ac_2O. Irrespective of the order of mixing the reactants, only the 2-haloethylthiol acetates are formed in this case



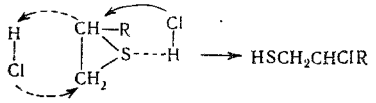
The diacetate of monothioethylene glycol was not isolated even in trace amounts. The reaction of ethylene sulfide with HCl in the presence of Ac_2O and AcOH is accompanied by oligomeric transformations



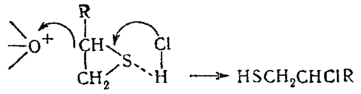
The obtained data testify to the fact that in low-polar media the cleavage of the thiirane ring by hydrogen halides does not proceed via the step of forming the carbonium cation. The ambiguous transformations of the thiiranes when reacted with hydrogen halides are probably related to the existence of several mechanisms, which lead to ring opening. The appearance of "normal" cleavage products in solvents that are inert toward hydrogen halides can be due to the formation and nucleophilic cleavage of the episulfonium ring by the halide anion from the state of an intimate ion pair



The "abnormal" opening of the ring in this case can proceed by the trimolecular mechanism via the intermediate π-complex

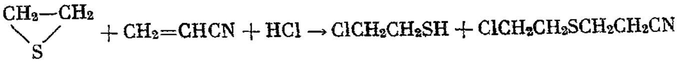


The possibility of cationic catalysis of the reaction in solvents that are inert toward hydrogen halides (water, ether) cannot be excluded



These concepts are in agreement with the data on the extremely low basicity of the sulfur atom of thiiranes, the high p-character of the heterobonds, and the similarity in the structure of their two-carbon skeleton to the double bond of alkenes. The latter apparently determines the similarity in the mechanisms of adding hydrogen halies to thiiranes and alkenes in nonpolar media.

To compare the nucleophilic properties of the thiirane ring and an activated double bond we studied the competing reactions in the system: ethylene sulfide–acrylonitrile–HCl. Of the possible reaction products only 2-chloroethyl mercaptan and 2-chloro-2'-cyanodiethyl sulfide were isolated in high yield



The latter testifies to the fact that the nucleophilic properties of the thiiranes are higher than those of an activated double bond.

EXPERIMENTAL METHOD

Reaction of THF with HCl. With stirring, dry HCl was bubbled at a slow rate into a mixture of 36 g of THF, 51 g of Ac_2O, and 60 g of AcOH to a weight increase of 15-16 g, with maintenance of the temperature at 45-60°C. Then the mixture was heated at 60° for 2 h and fractionally distilled. We obtained 8.3 g (11%) of 4-chlorobutyl acetate [12], bp 85-86° (14 mm); d_4^{20} 1.0267; n_D^{20} 1.4356, and 55.7 g (64%) of 1,4-diacetoxybutane, bp 117-119° (14 mm); d_4^{20} 1.0454; n_D^{20} 1.4226. Found: C 55.23; H 7.87%. $C_8H_{14}O_4$. Calculated C 55.10; H 8.05%.

From the residue by a double fractional distillation we isolated 7.9 g of 4-chloro-4'-acetoxydibutyl ether, bp 156-158° (14 mm); d_4^{20} 1.0465; n_D^{20} 1.4427 (Found: C 53.78; H 8.34; Cl 15.62%. $C_{10}H_{19}ClO_3$. Calculated C 58.64; H 8.55; Cl 15.76%), and 1.5 g of 4,4'-diacetoxydibutyl ether, bp 174-176°; d_4^{20} 1.0298; n_D^{20} 1.4341. Found: C 58.64; H 9.12%. $C_{12}H_{22}O_5$. Calculated: C 58.53; H 9.35%.

4-Chlorobutyl Acetate. With stirring, to a solution of 8-10 g of HCl in 51 g of Ac_2O at 0° was added 36 g of THF in drops, with the simultaneous bubbling in of dry HCl. At the end of exothermic reaction the mixture was slowly heated up to 55-60°, maintained at this temperature for 1 h, and then fractionally distilled. We isolated 56.4 g (75%) of product, bp 85-86° (14 mm).

2-Chloroethylthiol Acetate. Dry HCl was bubbled into a mixture of 6 g of ethylene sulfide and 20 g of Ac_2O at such a rate that the temperature of the reaction mass did not exceed 40-42°. At the end of exothermic reaction the mixture was heated at 45° for 1 h and then fractionally distilled. We isolated 10.4 g (74.9%) of product, bp 79-80° (20 mm); d_4^{20} 1.1730; n_D^{20} 1.4988. Found: Cl 25.37; S 23.21%. C_4H_7ClOS. Calculated: Cl 25.60; S 23.10%.

Under similar conditions were obtained β-bromoethylthiol acetate [13] in 79% yield, bp 92-93° (20 mm); d_4^{20} 1.5328; n_D^{20} 1.5228, and β-bromethylthiol-2,4-dichlorophenoxyacetate in 68% yield, mp 34°. Found: S 9.42%. $C_{10}H_9BrCl_2O_2S$. Calculated: S 9.30%.

2-Chloroethyl Mercaptan and 2-Chloro-2'-cyanodiethyl Sulfide. With stirring and cooling, dry HCl was bubbled into a solution of 6.0 g of ethylene sulfide and 5.3 g of acrylonitrile in 30 ml of benzene to a weight increase of 3.5-3.6 g, maintaining the temperature of the reaction mass below 20°. Then the mixture was stirred at 20° for 1 h, at 60-70° for 3 h, and fractionally distilled. We obtained 3.67 g (38%) of 2-chloroethyl mercaptan [14], bp 38-39° (40 mm); n_D^{20} 1.5824 and 6.31 g (42.3%) of 2-chloro-2'-cyanodiethyl sulfide, bp 130-132° (4 mm); d_4^{20} 1.1998; n_D^{20} 1.5346. Found: N 9.15; Cl 23.29; S 21.28%. C_5H_8NClS. Calculated: N 9.38; Cl 23.42; S 21.37%.

CONCLUSIONS

A study was made of the reactions that proceed in the systems: THF–hydrogen halide–acetic anhydride and ethylene sulfide–hydrogen halide–acetic anhydride. The cleavage of the THF ring most probably proceeds via the step of forming carbonium ions. The data on the transformations of ethylene sulfide are in agreement with the concepts of bi- and trimolecular processes for the cleavage of either the episulfonium ring or the activated thiirane ring by either hydrogen halide or halide anion from the state of an intimate ion pair.

LITERATURE CITED

1. W. Davies and W. E. Sawide, J. Chem. Soc., 317 (1950).
2. W. Davies and W. E. Sawide, J. Chem. Soc., 771 (1951).
3. C. C. J. Culvenor, W. Davies, and N. S. Heath, J. Chem. Soc., 282 (1949).
4. J. M. Stewart, J. Org. Chem., 28, 596 (1963).
5. G. Yu. Épshtein, I. A. Usov, and S. Z. Ivin, Zh. Obshch. Khim., 33, 3638 (1963).
6. N. V. Schwartz, J. Org. Chem., 33, 2895 (1968).
7. M. G. Lin'kova, Dissertation [in Russian], Moscow (1972).
8. A. Oddon and J. Wylde, Bull. Soc. Chim. France, 1607 (1967).
9. E. van Tamelen, J. Am. Chem. Soc., 73, 3444 (1951).
10. M. Delepine, Compt. Rend., 171, 36 (1920).
11. M. Delepine, Bull. Soc. Chim. France, (4), 27, 740 (1920).
12. R. Paul, Bull. Soc. Chim. France, (5), 6, 1162 (1939).
13. S. Z. Ivin, Zh. Obshch. Khim., 28, 177 (1958).
14. E. M. Meade and F. N. Woodward, J. Chem. Soc., 1894 (1948).