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# INTRAMOLECULAR ADDITIONS OF SULFENYL CHLORIDES

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It has long been invoked that the additions of sulfenyl halides to olefins occur in ionic mechanism as intervening an episulfonium ion[1]. This ionic process may be responsible for trans additions, but not for anti-Markovnikov additions. Since neighboring $\beta$-S-participation in solvolysis has been well established as processes via episulfonium intermediates[2], it is noteworthy, in order to further clarify the reaction processes of sulfenyl halide additions, that the results of the additions are compared with those of solvolysis in same systems. Thus, we wish to report here the results of the intramolecular additions of 4-pentenesulfenyl chloride (3a) and 4-methyl-4-pentenylsulfenyl chloride (3b).

Disulfides (2a,2b) were synthesized from the reaction of tosylates (1a,1b), which were obtained by the tosylation of the corresponding alcohols[3,4] with sodium disulfide: 2a; bp 102-103°/5 mmHg, $n_D^{20}$ 1.5145. Mass spectrum m/e (%); 202 (0.5,$M^+$), 101 (85,$M^+/2$), 69 (53,$C_5H_9^+$), 41 (100,$C_3H_5^+$). 2b; bp 115-117°/3 mmHg, $n_D^{20}$ 1.5134. Mass spectrum m/e (%); 230 (0.1,$M^+$), 115 (100,$M^+/2$), 55 (54,$C_4H_7^+$). The cleavage of the disulfides with halogen was carried out in chloroform with 1 mequiv of chlorine gas at -30°.[5] Resultant sulfenyl chlorides (3), whose isolation failed because of their instabilities, cyclized readily to 5- and 6-membered ring compounds (4,5)[6]. This provides good evidence that the intramolecular addition is extremely fast. The ratios of the initial products were determined by glpc analysis of sulfones (6,7) derived from m-chloroperbenzoic acid (MCPBA)-oxidation because 4 and 5 are thermally interconvertible isomers. The skeletal rearrangement of 4 to 5 took place easily even on standing the reaction mixture at room temperature. Accordingly, direct analysis of the initial products (4,5) by glpc or pmr led to wrong results. The ratios of the initial and rearranged products are summarized in Table I[7]. Past observation detected only anti-Markovnikov adduct in similar additions[8], may result from processes which are different from the present

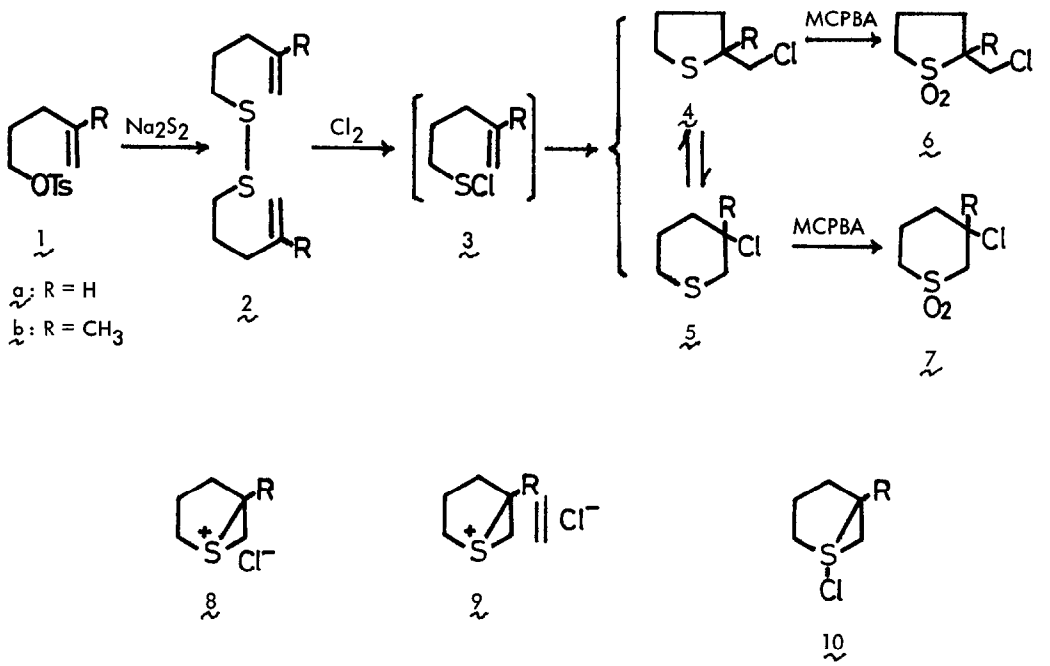


Table I. Relative Yields of Products[a]

| Compd | % Product ratio — Initial 4 | Initial 5 | Rearranged 4 | Rearranged 5 |
|---|---|---|---|---|
| 3a | 79.6 | 20.4 | 18.1 | 81.9 |
| 3b | 95.4 | 4.6 | 4.4(3.1)[b] | 95.6(96.9)[b] |

a, Ratios were determined by glpc analysis of 6 and 7. b, Ratio obtained by integrating the methyl signals of 4b and 5b in pmr spectra.

cases.

As is shown in Table I, the intramolecular additions in both systems gave anti-Markovnikov isomers mainly and interestingly a methyl substituent increased its selectivity. If the addition involves an episulfonium ion as intermediate, opening must direct to the formation of anti-Markovnikov-oriented isomer, which is opposite to opening of a usual episulfonium ion formed in solvolysis. This discrepancy has been interpreted in terms of the difference of ion pairs ( a tight ion pair (8) and a solvent separated ion pair (9) ) or a tetravalent intermediate (10).[1b,9]

Thermal equilibrium between 4 and 5, isomer distribution depending on thermodynamic stabilities, resulted in the 6-membered rings (5) as a major isomer, which were consistent with the product ratios in solvolysis of the two sets of the related compounds: 4a and 5a (Cl=OPNB), in hydrolysis, gave the same products in a same ratio ( 4a : 5a (Cl=OH)=18 : 82 )[2] and product ratio in the solvolysis of 4b and 5b (Cl=OPNB) was 4b : 5b (Cl=OH)=2 : 98.[10] These facts indicate that the rearrangement step would involve a similar episulfonium ion to solvolysis.

Although the data of both processes, addition and rearrangement, are compatible with episulfonium ion intermediates, it seems likely that they are originally different. The addition proceeds via an episulfonium ion derived from the electrophilic attack of $RS^+$ to a $\pi$-bond, while the rearrangement involves it produced by the nucleophilic attack of divalent sulfur. This difference in origin brings about different types of episulfonium ions, as with charge localized on sulfur and charge delocalized over carbon, which undergo the opening to result in opposite isomer distribution. The former may be a stiff episulfonium ion which is energetically unstable and generally involved in reactions of sulfenyl chloride additions or ring openings of epoxides,[11] while the latter may be a charge-delocalized, soft episulfonium ion, which is relatively stable and is intermediates of solvolysis, isomerization of $\beta$-chlorosulfides and related reactions. Substituents such as phenyl or vinyl lead to the latter ion because they highly stabilize a carbocation.[12] We are currently investigating the effects of substituents and stereochemistry in intramolecular additions in order to obtain further evidence of the mechanism and synthetic values of S-containing heterocycles.

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5. Calculated amount of chlorine gas was introduced to a solution of disulfide in chloroform by the aid of a hypodermic syringe.

6. Evidence that the initial attack of chlorine took place on a disulfide group rather than a double bond, resulting cleavage of a S-S bond, was obtained from similar reactivities of both compounds ( $k_{Me}/k_H=1.2$ ). It has been reported that the electrophilic addition of chlorine to isobutylene occurs at 50 times faster rate than 1-butene ( M.L.Poutsma, Science, 157, 997 (1967) and also see W.H.Thaler, J. Org. Chem., 34, 871 (1969) ).

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