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Quantum-chemical Analysis of Reactions between Alkenes and Sulfenyl Chlorides. Position of Episulfuran and Tight Ion Pair on the Reaction Coordinate

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Abstract—In the first stage the reaction between 3,3-dimethyl-1-butene and 1-phenyl-5-tetrazolylsulfenyl chloride gives rise to intermediate of tight ion pair type that, in the course of system movement along the reaction coordinate, transforms into an intermediate species of sulfuran type or directly into an adduct. The intermediate of sulfuran type also transforms into an adduct going over the energy barrier of 40 kcal mol^{-1}. The formation of an episulfuran type intermediate directly from the reagents requires overcoming an energy barrier that is by 10 kcal mol^{-1} higher than in going through a tight ion pair.

A significant progress was achieved within the last decades in understanding the mechanism and in performing uncommon reactions of alkenes with sulfur-containing electrophiles. The most important among the latter are sulfenyl halides and their analogs with similar electrophilic part [1, 2]. Under usual conditions the reactions of alkenes with these reagents occur virtually in a single direction to yield addition products (addition direction). Therefore the reagents were classed with the group of typical weak electrophiles [3]. It was universally accepted [4] that the adducts are formed via intermediates of episulfonium ion A type (Scheme 1).

Scheme 1.
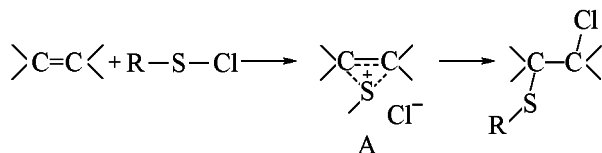
The concept is illogical since in the intermediate with a high degree of charge separation as in the episulfonium ion the only possible transformation direction would be the flapping of one of the electron-deficient centers in the A species with its own nucleophile. The existing views on this mechanism underwent later radical corrections [1, 5].

According to the concept in question the addition direction occurs via intermediate species of episulfuran B type or tight ion pair C, and the nonadditive transformations (skeleton rearrangements,

cyclizations, deprotonation etc.) proceed through intermediates of episulfonium ions A type [1, 5, 6].
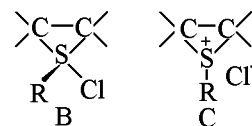
Thus the nonadditive directions in reaction between unsaturated compounds and sulfur-containing reagents are induced by creating conditions that ensure formation of intermediates with relatively high degree of charge separation. This is achieved by coordination of the reagent with electron-with-drawing components prior to reaction (increasing of the reagent electrophilicity) [7], and/or by charge separation in the intermediates effected by strong electrolytes, e.g., by replacing the proper nucleophile by a coordinationally saturated counter-ion (increasing of the effective electrophilicity) [1, 8].

The results of ab initio calculations [9] for the reaction of ethylene with mercaptosulfenyl chloride suggest that in the first stage a carbocationic species of episulfuran B type is generated that in the course of further motion along the reaction coordinate is transformed into episulfonium ion A.

The direct formation of episulfuran B from the reactants is actually a cycloaddition that is hampered by significant steric hindrances due to the rigid orientation of the approaching partners. The expected high energy barrier is presumably notably under-
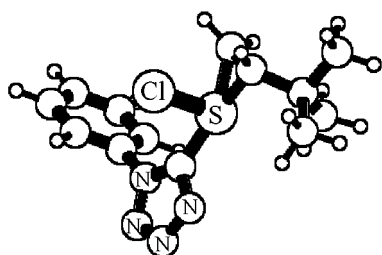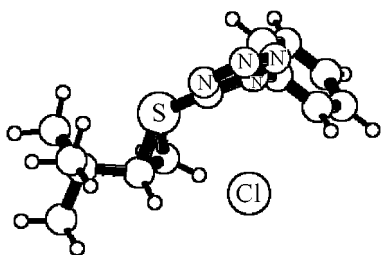
Fig. 1. Structure of transition state D.

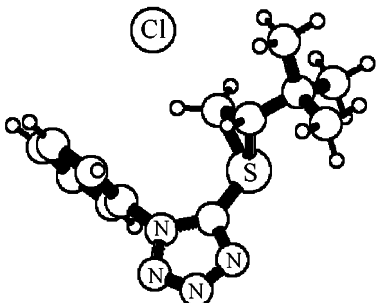**Fig. 2.** Structure of tight ion pair E.

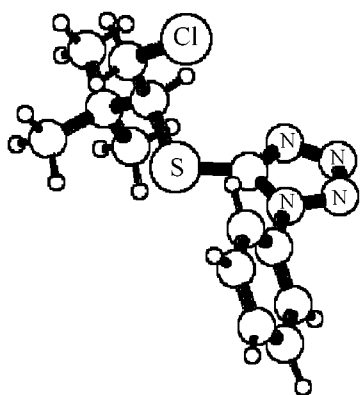

Fig. 3. Structure of transition state F.

Fig. 4. Structure of adduct **III**.

estimated in [9] because of simplified models of substrate and reagent taken into consideration. No geometry optimization of the reacting system during its motion from the initial to final state also may provide fairly inaccurate results.

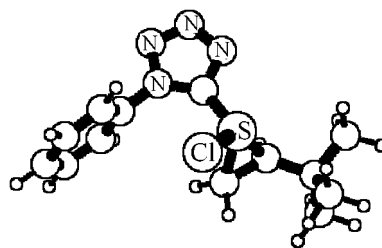Taking into account the great theoretical and practical importance of reaction between alkenes and

Fig. 5. Structure of sulfuran G.

bivalent sulfur we carried out calculations by MNDO procedure for a reaction of 3,3-dimethyl-1-butene (**I**) with 1-phenyl-5-tetrazolylsulfenyl chloride (**II**). The calculations were carried out in the s,p,d-basis with the use of MNDO-92 software [10] with full geometry optimization of the reacting system.

The calculation with full optimization of the system geometry revealed that at approach of the molecules of sulfenyl chloride and alkene till 2 Å distance the reagent is directed to the terminal carbon atom of the double bond in the alkene **I**. In this situation the forced rupture of the S–Cl bond results in a sharp increase in the system energy (energy barrier over 130 kcal mol^{-1}) with replacement of a methylene hydrogen in the substrate by the electrophilic part of the reagent followed by hydrogen chloride elimination.

When the electrophilic center of the reagent attacks the substrate normal to the alkene double bond at its center (Fig. 6, stage 1a) the system arrives to the transition state D (energy barrier 72 kcal mol^{-1}) of cyclic structure with four-coordinate sulfur atom located in the same plane as the adjacent carbons. Then the system transforms into an intermediate of a type of tight ion pair E with no covalent bonding between the counter-ions as shows Wiberg index.

The fate of the reacting system is determined by the direction of counter-ions reaction during the further motion of the intermediate E along the reaction coordinate. The displacement of chloride anion to the rear side of the thietane ring with respect to the sulfur atom affords the transition state F (energy barrier no more than 10 kcal mol^{-1}) of structure similar to that of episulfonium ion. This uncommon state of the reacting system at insignificant compulsory changes in its geometry mostly connected with motion of the chloride anion is easily transformed into three local minima: into a tight ion pair E (approach of the chloride anion to sulfur, stage 2); into anti-Markownikoff adduct **III** (flapping of the electron-deficient center, stage 1b), and into an intermediate of sulfuran type G (covalent bonding with the sulfur atom, stage 3a).
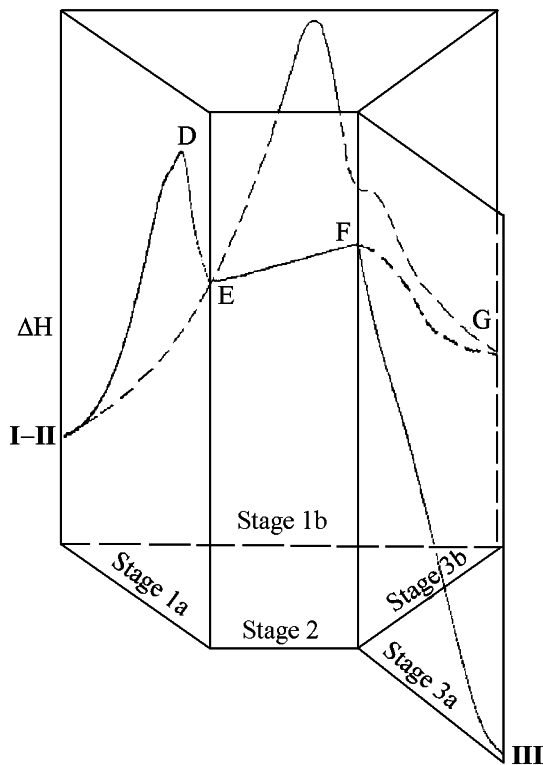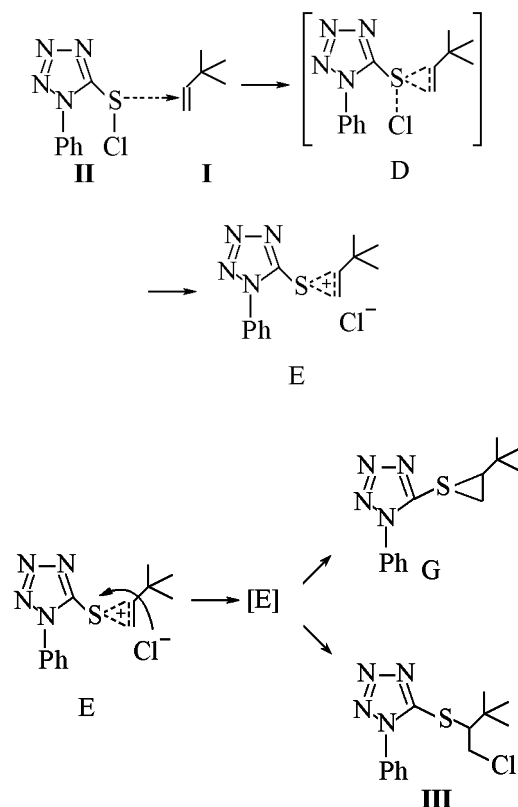
Fig. 6. Section of potential energy surface for reaction of 1-phenyl-5-tetrazolylsulfenyl chloride with 3,3-dimethyl-1-butene.

Scheme 2.

In the light of [8, 9, 11] the most crucial is the problem of sulfuran structure, its location of the reaction coordinate, and its role in distribution of the reaction products. Therefore we carried out the analysis of the route of sulfuran formation directly from reagents using the characteristics obtained for sulfuran G.

The approaching of reagents was performed at fixed values of bond and torsion angles in the S–Cl fragment with respect to carbon atoms of the double bond. The corresponding values were taken from the geometry found for the intermediate G. The reacting system furnished sulfuran without preliminary rupture of the S–Cl bond (stage 1b). However the energy barrier on this route of sulfuran G formation is by over 10 kcal mol^{-1} higher than in two-stage sulfuran formation via tight ion pair (stages 1a, 2, 3a).

Thus basing on the calculations performed the mechanism of reaction between alkenes and compounds of bivalent sulfur may be represented by Scheme 2.

The above scheme introduces important corrections into the existing views on alkenes reactions with compounds of bivalent sulfur. The most significant among them are the positions of the tight ion pair, sulfuran, and episulfonium ion on the reaction coordinate. Although the transition state D by coordination number of the sulfur atom is like sulfuran, the location of the transition state (the peak of the barrier) and the geometry of placement of substituents at the sulfur atom (planar structure) are not similar to a species of sulfuran G type. Actually the formation of such intermediate is preceded by a tight ion pair that is virtually responsible for the routes leading to final adducts, and therewith the central position of these routes is the transition state E; from this transition state the system moves to local minima by several directions.

The results obtained provide a good illustration of the predominance of addition direction in reactions of alkenes with compounds of bivalent sulfur. The energy barrier corresponding to this direction is considerably lower (72 kcal mol^{-1}) than that of a reaction characteristic of strong electrophiles, replacement of hydrogen in alkene by the electrophilic part of the reagent, where the energy barrier of the limiting stage is over 130 kcal mol^{-1}.

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