Russian Journal of General Chemistry, Vol. 71, No. 5, 2001, pp. 729–735. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 5, 2001, pp. 776–784.

Types, Symbolism of Representation of Steric Structure, and Conformations of Ion Pairs. Stereochemical Version of the Generalized Rule of Elimination

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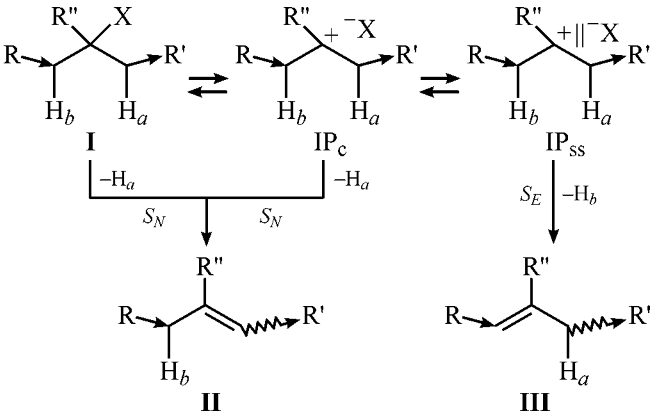
Received November 9, 1999

Abstract—Analysis of published data from the standpoint of the generalized rule of elimination demonstrated that in addition to contact and solvent-separated ion pairs, in elimination a species of a third type is generated, called spatially separated ion pair. This is an intermediate formed on the pathway of transformation of a contact ion pair to a solvent-separated one. Each of these ion pairs preserves its initial configuration of the bond C–nucleofuge starting from its origination to transformation into an elimination product, demonstrating discrete and inherent regio- and stereoselectivity: a contact ion pair shows nucleophilically controlled *syn* reactivity, and spatially- and solvent-separated ion pairs, electrophilically controlled *syn* and *anti* reactivity, respectively. The generalized rule of elimination allows almost faultless prediction of regio- and stereoselectivity, being applicable to interpretation of even those published data which appear surprising or abnormal from the standpoint of the modern theoretical views.

Analysis of published data [1–8] shows that the generalized rule of elimination proposed recently [9] is best suited for prediction of regioselectivity of elimination. According to this rule, compounds **I** enter elimination reactions immediately or after generation of ion pairs C–X (C–nucleofuge) (Scheme 1). In this case alkenes **II** are formed both from **I** and its contact ion pair (IP_c), while alkenes **III**, only from a solvent-separated ion pair (IP_{ss}).

Scheme 1.



R is an electron-donor substituent, R' is an electron-acceptor substituent, R" can be any substituent, H_a is a more acidic hydrogen atom, H_b is a less acidic hydrogen atom, and X is a nucleofuge.

Contrary to the Zaitsev's and Hofmann's rules or the variable transition state theory [1–8], the proposed generalized rule has practically no exceptions, which considerably facilitates synthetic design and solution of other theoretical and practical problems [9–15]. However, analysis of published data [1–8, 16–27] revealed that the generalized rule exactly predicts the path, but not stereochemistry of elimination. This fact casts doubt on the correctness of those stereochemical characteristics that are mostly attributed to ion pairs. Thus, it is known that reactions of contact ion pairs with nucleophiles [1–8, 25–29] are usually accompanied by inversion of the conformation at the carbon atom associated with X, and also it is assumed that deprotonation (elimination) involves the most acidic proton by a *syn*-elimination path. In the case of solvent-separated ion pairs the reaction with nucleophiles is accompanied by only partial inversion, so that a racemate is formed when an optically active substrate is used; deprotonation proceeds as *anti* elimination, i.e., it is assumed that the solvent-separated ion pair behaves like a carbocation having a planar structure.

Therefore, we made re-examination of a series of data on stereochemistry of solvolytic elimination and related processes, i.e., of the reactions in which precursors of the elimination products would be only ion pairs or free carbocations, but not the corresponding neutral molecules.

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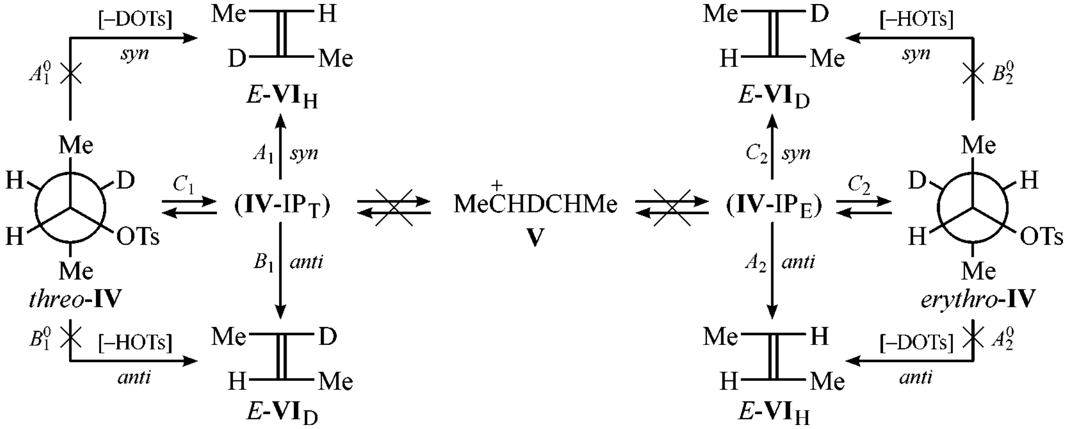
Scheme 2.



There are a lot of data [16–24] which directly or indirectly support the validity of our doubts. In this connection the most useful information is found in the papes [21] devoted to solvolytic elimination reactions of 3-deutero-2-butyl tosylates. It was demonstrated that in solvolytic elimination the *threo* and *erythro* tosylates **IV** are not transformed each to other, but deuterated and undeuterated (*E*)-2-butenes **VI** are formed (Scheme 2). Since the alkenes cannot be formed under these conditions directly from the neutral molecule **IV**, this leaves as the only alternative the conclusion that the only precursors of isotopological (*E*)-2-alkenes **IV** are ion pairs **IV**-IP. In other words, although in solvolytic elimination intermediate ion pairs **IV**-IP are generated, they are not transformed to intermediate carbocation **V** common for both stereomers. It was demonstrated also that each of the stereoisomeric tosylates yields a mixture of all possible (deuterated and undeuterated) isotopomers of (*E*)-2-butenes **VI**, whose proportion depends on a solvent used: in weakly polar solvents deprotonation (dedeuteration) proceeds highly stereoselectively by the *syn* path, and in more polar solvents, highly stereoselectively too, but by the *anti* path. Note that in both cases *syn* and *anti* deprotonation proceeds so as it would occur in the starting neutral molecule **IV** (compare pathways *A*, *B*, and *C* in Scheme 2). For example, alkene *E*-**VI**$_H$ is generated from *threo* tosylate **IV** through *syn* deprotonation of ion pair **IV**-IP$_T$, and alkene *E*-**VI**$_D$, from the same ion pair, but through *anti* deprotonation. Elimination of the proton or deuteron from ion pair **IV**-IP$_E$ proceeds similarly. Combination of these data suggests that over the timeline from the origination of the ion pairs to their transformation into isomeric 2-alkenes, the ion pairs preserve that configuration of the C–nucleofuge bond which was in the initial molecule before it was transformed to any of the ion pairs.

The cited paper [21] provides also an important information on the nature of ion pairs subjected to deprotonation to yield isotopic 2-alkenes **VI**. It seems at first glance that, since the same isotopic alkenes **VI** (*E*-**VI**$_H$ and *E*-**VI**$_D$), depending on the substrate nature (*threo*-**IV** or *erythro*-**IV**), are formed by both *syn*- and *anti*-elimination paths, the precursors of the *syn*- and *anti*-elimination products may be suggested to be contact and solvent-separated ion pairs, respectively. However, it follows from the published results [1–8, 16–29] and the generalized rule of elimination (see above) that this is a mistaken belief, as a characteristic indication of a contact ion pair, in addition to *syn* deprotonation, is participation in this process of a more acidic hydrogen atom H$_a$ of the system (Scheme 1). Therefore, if in this case a particle having the features of a contact ion pair were formed, its deprotonation should involve more acidic hydrogen atoms of the methyl group, but not less acidic hydrogen atoms of the methylene group. Also we excluded from our analysis the possibility of formation of both *syn*- and *anti*-elimination products (for example, of alkenes *E*-**VI**$_H$ and *E*-**VI**$_D$ in the case of *threo*-**IV** isomer or alkenes *E*-**VI**$_D$ and *E*-**VI**$_H$ in the case of *erythro*-**IV** isomer) from the same solvent-separated ion pair. This conclusion is supported by the fact that the *E*-**VI**$_H$/*E*-**VI**$_D$ and *E*-**VI**$_D$/*E*-**VI**$_H$ alkene molar ratios do not remain unchanged, but vary as the reaction conditions or the nucleofuge change. Therefore, one may suggest that this point gives an evidence in favor of the fact that the *syn* deprotonation under consideration involves some species whose regiochemistry is similar to that of IP$_{ss}$, and stereochemistry, to IP$_c$. It follows from the results obtained in [20] that such a species is most likely formed as an intermediate on the path of transformation of IP$_c$ to IP$_{ss}$. Although a species with the indicated characteristics is not found in the literature, there is some indirect evidence that it was detected for the first time and described in the works [28, 29] devoted to nucleophilic substitution reactions. The authors called this species spatially separated ion pair (IP_{sps}). In view of clear analogy between the genesis of this species and the species we identified in our analysis (the indicated species is generated after IP_c, but before IP_{ss}), we will call it IP_{sps} too.

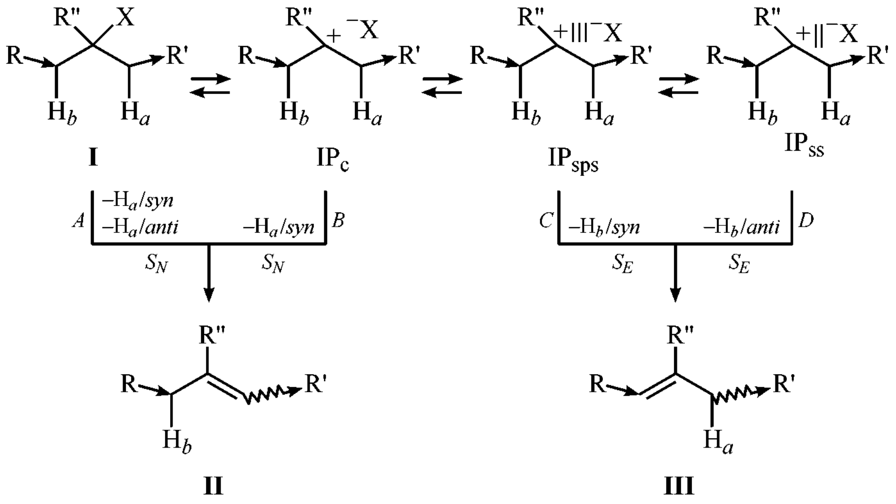
As known [1–8], this approach to recognition and registration of the intermediate species was proposed and then widely used by Winstein [25], Cram [16, 17], Bordwell [30], and other apologists of the concept of ion pairing in organic chemistry. Indisputable preference of this approach is that it provides information about donor–acceptor interaction occurring at the molecular level, which is practically inaccessible for other related methods.

Therefore, one may conclude from the above considerations that each of the solvolytic elimination paths is caused by generation and consumption of a specific type of ion pair: in the case of IP_c products are formed through elimination of more acidic hydrogen atom, and in the cases of IP_{ss} and IP_{sps}, less acidic hydrogen atoms of the three-carbon system (Scheme 1); IP_c and IP_{sps} are deprotonated by *syn*-, and IP_{ss}, by *anti*-elimination path.

Our thought is that the identification of the third type of ion pair (IP_{sps}) in elimination reactions is not only a confirmation of a specific fact previously reported for nucleophilic substitution reactions, but a some fundamental phenomenon. In other words, some indications of origination and consumption of spatially separated ion pairs should be found also in addition and rearrangement reactions.

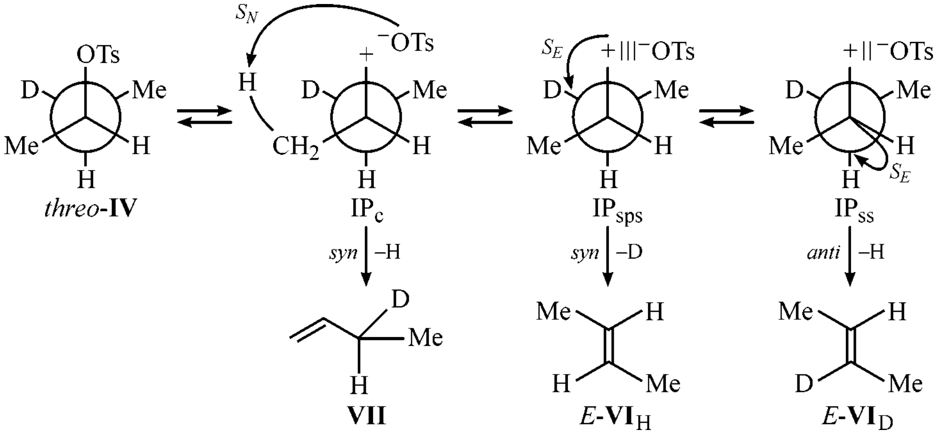
In the light of the above considerations, the symbolism of representation of the structure and configuration of ion pairs becomes questionable. Indeed, the potentialities of the existing symbolism [1–10, 16, 21, 25, 26, 28, 29] have been exhausted after it became clear that the bond C–nucleofuge in ion pairs has the same steric orientation as in the initial molecule. Therefore, our thought is that such a new symbolism has to be developed, which would allow representation of the indicated fundamental property of ion pairs so easily as it is realized in the case of molecules with covalent bonds. Of course, this information could be represented by drawing orbitals [1–8, 32–36], but we believe that more preferable symbolism is that combining the commonly accepted simplicity with the clearness of the orbital representation. This can be realized, for example, with a modified scheme illustrating the generalized rule of elimination (Scheme 3; R, R', R" and X are the same as in Scheme 1).

Scheme 3.



Now it becomes possible to say about not only the steric structure, but also about the conformations of each of the ion pairs using Newman projections. As an illustration, below is given an example of representation of one of the conformations of IP_c, IP_{sps}, and IP_{ss} originated from tosylate *threo*-**IV** (Scheme 4).

Scheme 4.



Arrows in the scheme demonstrate what fragment of the ion pairs plays a role of a real reactant initiating attack to the substrate from the *syn* or *anti* position against its nucleofuge, and the symbols S_N and S_E reflect the nature (nucleophilic and electrophilic, respectively) of the attacking agent.

To illustrate the universal nature and high prognostic power of these principles of the generalized rule of elimination, below we offer reinterpretation of a series of reactions whose regio- or stereoselectivity appears strange or illogical.

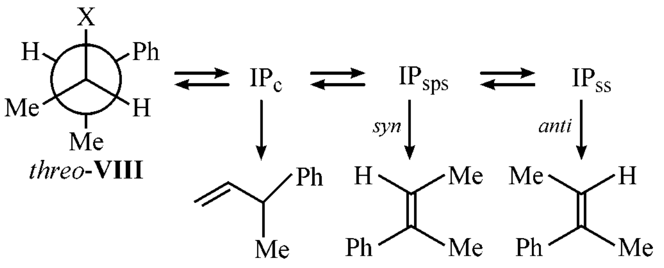
So, if regio- and stereochemistry of a reaction could be really predicted on the basis of these principles, then changing of a good nucleofuge for a bad one and vice versa should initiate shifting of the equilibrium of ion pairing to the left, changing the proportion of the corresponding stereo- and regioisomeric alkenes to the theoretically expected direction.

Indeed, this statement has been confirmed by analysis of a great body of published data [4, 5, 8, 9, 16–24]. Thus, 3-phenylbutyl tosylates and brosylates **VIII** (*threo* isomer is shown in Scheme 5) in solvolytic reactions, in addition to 3-phenyl-1-butene **IX** (it is formed in part by rearrangement of the reaction intermediates [20]), yield a mixture of alkenes **X** and **XI**.

Changing the tosylate for a more readily leaving group (brosylate) increases the yield of **XI** formed by the *anti*-elimination path. In the case when the tosylate group is changed for a hardly leaving group, for example, dimethylaminoxide group, the ion-pairing equilibrium, most likely, shifts to the left (fraction of IP_{sps} increases), and the 2-alkene is formed by the *syn*-elimination path [17].

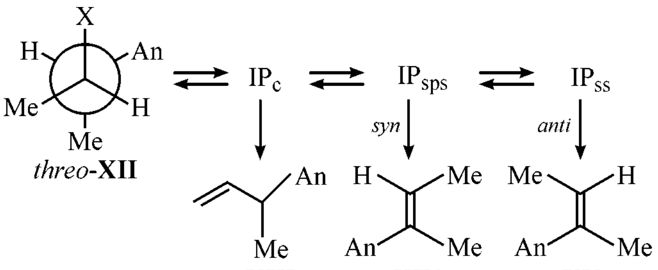
In a series of works [4, 5, 7, 8, 32–37] it was demonstrated that such weak bases as thiophenoxide and chloride ions in polar aprotic solvents initiate rapid elimination of HX. Now this type of reactions is known as E_2C elimination, which, according to Bunnet [37], represents a special kind of concerted E_2 elimination. Such a reaction occurs with cyclic and acyclic molecules containing various leaving groups [22]. An example of such elimination is fragmentation of *threo*-3-*p*-anisyl-2-butyl chloride **XII** (*threo*-**XII**, X = Cl) in the presence of tetrabutylammonium chloride in acetone at 75°C. In this case stereoisomeric alkenes **XIV** and **XV** are formed (Scheme 6).

Scheme 5.



	IX	*E*-**X**	*E*-**XI**
X = OTs	6.5%	41%	29%
OBs	10%	25%	54%
NMe_2	14.5%	86–95%	0%

Scheme 6.

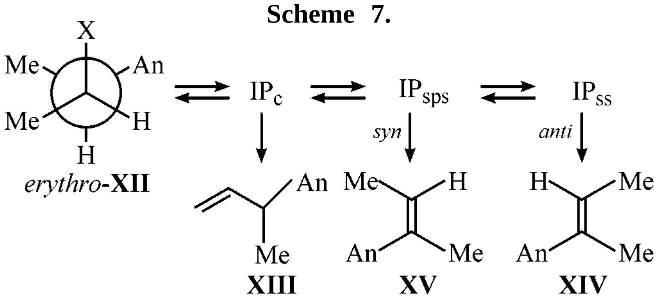


	XIII	**XIV**	**XV**
X = Cl	none	20%	80%
OBs	none	1%	99%

An = *p*-anisyl.

Similar reaction of the *erythro* isomer (*erythro*-**XII**, X = Cl) with the same tetrabutylammonium chloride in acetone at 50°C yields (in addition to 9.3% substitution product) 1-alkene **XIII** (3.9%) and the same alkenes **XIV** and **XV**, but in the 95 : 5 ratio, which corresponds to 82 and 4% yields (Scheme 7). Changing chloride for the brosylate group (X = OBs) in the *threo* and *erythro* isomers **XII**, thanks to a better nucleofugacity of the latter, increases the contribution of *anti* elimination to 99 : 1 for both molecules (see above).

Scheme 7.



	XIII	XV	XIV
X = Cl	4%	4%	82%
OBs	none	1%	99%

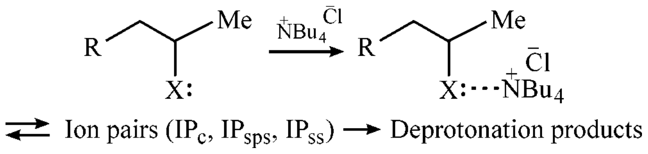
An = *p*-anisyl.

Evidently, the precursor of alkene **XIV** is IP$_{sps}$ in the case of the *threo* isomer, and IP$_{ss}$, in the case of the *erythro* isomer, and vice versa, the precursor of alkene **XV** is IP$_{ss}$ in the case of the *erythro* isomer, and IP$_{sps}$, in the case of the *threo* isomer (Scheme 7). Similar case was described in [22] for E_2 reactions of cyclic compounds with tetrabutylammonium chloride.

It is logical to suggest that in these elimination reactions the precursors of the resulting stereoisomeric alkenes are species having the properties of spatially and solvent-separated ion pairs.

Evidently, the true mechanism of E_2C elimination resembles the mechanism recently proposed for phase-transfer catalytic reactions [15]. In other words, elimination occurs as, thanks to interaction of a positively charged nitrogen atom (in tetrabutylammonium chloride) with a nucleofuge of a substrate, the C–N$^+$ bond is subject to heterolysis, and generation of ion pairs (IP$_c$, IP$_{sps}$, and IP$_{ss}$) proceeds (Scheme 8), which are deprotonated then in full agreement with principles of the generalized rule of elimination.

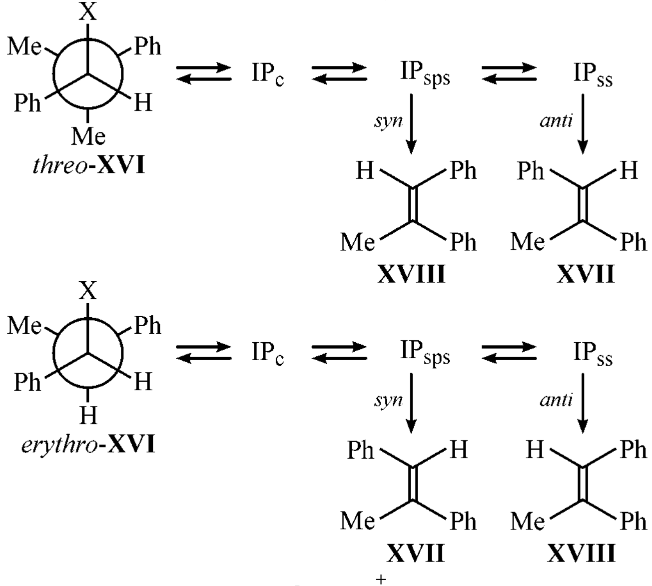
Scheme 8.



Similar situation arises in the case of reactions proceeding by the E_2 mechanism (E_2H elimination). Evidently, this can be due to the fact that even under conditions of bimolecular elimination it is impossible to avoid formation of intermediate ion pairs and their subsequent transformation to stereoisomeric alkenes [4, 5, 9].

As an illustration of this concept, below we consider results of one of the most thorough study of the stereochemistry of elimination, performed by Cram [38]. This study was devoted to elimination in *threo*- and *erythro*-1-X-1,2-diphenylpropanes **XVI** (*threo*-**XVI** and *erythro*-**XVI**) in reactions with a wide spectrum of bases. It was demonstrated that in the presence of primary and secondary sodium alkoxylates (in the corresponding alcohol), a clearly pronounced *anti* stereoselectivity of elimination is realized: from *erythro*-**XVI** (X = Cl) *Z*-alkene **XVIII** (*anti*-elimination product, i.e., the product of transformation of IP$_{ss}$) is formed; and from *threo*-**XVI** (X = Cl), alkene **XVII**, i.e., again the product of transformation of IP$_{ss}$. However, in a mixture of potassium *tert*-butylate with *tert*-butanol, i.e., in a less polar solvent than in using primary alcohols, these chlorides react by the *syn*-elimination path (in other words, the products of transformation of IP$_{sps}$ are formed). As would be expected, contrary to the chloride (*threo*-**XVI**, X = Cl), the bromo derivative (*threo*-**XVI**, X = Br) preferentially forms *E*-alkene **XVII** (product of *anti*-elimination, i.e., the product of transformation of IP$_{ss}$) even in the mixture of potassium *tert*-butylate–*tert*-butanol, since Br is a stronger nucleofuge than Cl. Compound *erythro*-**XVI** (X = N$^+$Me$_3$), in which the C–N$^+$ bond is even less prone to heterolysis than the C–Cl bond, yields *E*-alkene **XVII**, i.e., the deprotonation product of IP$_{sps}$, only. These results are summarized in Scheme 9.

Scheme 9.

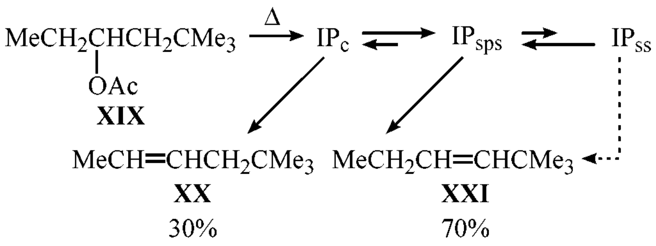


X = Cl, Br, $\overset{+}{N}Me_3$.

In other words, the trend is that the proportion of stereoisomeric alkenes (**XVII** and **XVIII** in this case) changes in parallel to the easiness of generation of the corresponding ion pairs (IP_{sps} and IP_{ss}); under favorable conditions for generation of IP_{sps}, the product of its deprotonation is formed, and vice versa.

Using similar approach one may interpret regio- and stereoselectivity of other types of elimination reactions: fragmentation of xanthates and esters by Tschugaeff, of aminoxides by Cope, etc. [4, 5, 39, 40]. Indeed, it is well known [41, 42] that the rates of pyrolysis of cholesterol esters linearly depend on pK_a (on the nucleofugacity by the essence) of the corresponding carboxylic acids: electron-acceptor substituents in the acid fragment of the molecule facilitate elimination in consistence with the principles of polar elimination. This similarity was indicated by Maccoll as early as in late 1950s [43]. Most likely, the only difference of this type of elimination from the classic one is that in the series of the indicated compounds the leaving groups have a lower nucleofugacity as compared to the molecules which are prone to enter the truly polar elimination reaction. Evidently, by virtue of this fact, under conditions of thermal fragmentation, heterolysis of the bond C–nucleofuge is confined to generation of species with the properties of IP_c and IP_{sps}. A clear evidence in favor of this approach to interpretation of the reaction mechanism is given by the examples of thermal fragmentation presented below. Also these examples confirm the view that the commonly accepted mechanism of such fragmentation, ostensibly proceeding through 5- or 6-membered transient states, in fact does not occur; if such kind of interaction were realized (E_2H), only the more acidic hydrogen atom neighboring to the nucleofuge should be eliminated. However, in fact, it is not infrequently that the less acidic hydrogen atom is eliminated; this occurs just under conditions allowing heterolysis of the bond C–nucleofuge (for example, by introduction of an electron-donor substituent or a stronger nucleofuge). Most likely, in this case IP_{sps} or even IP_{ss} is generated, and deprotonation products of these ion pairs are predominantly formed (Scheme 10).

Scheme 10.



For instance, in fragmentation of acetate **XIX**, the major product is alkene **XXI**, and alkene **XX** is only the minor product [44]. Similar trends are observed in a series of cyclic and acyclic compounds [45, 46].

Thus, it becomes clear from the above considerations that the approach proposed demonstrates a considerably higher predicting power as compared to well-known approaches. It provides a basis for prediction and interpretation of even those experimental data [1–8, 19, 43, 47–49] which appear abnormal or unexpected from the standpoint of the modern theoretical concepts. But the most significant advantage of this approach is that it may be expanded to organic reactions other than elimination. Among them are addition to the carbonyl group, cleavage of the oxirane ring, rearrangements, etc. Most likely, this is caused by the fact that ion pairs, regardless of the reaction type and method of their generation, demonstrate the same behavior. This means that the ion-pair concept opens a door for solving various theoretical and practical problems of the organic chemistry. These problems will be considered in more detail in the subsequent communications.

ACKNOWLEDGMENTS

The authors are grateful to I. Cunningham (University of Surrey, the United Kingdom) for useful discussions.

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