Episulfonium Ions: Myth and Reality

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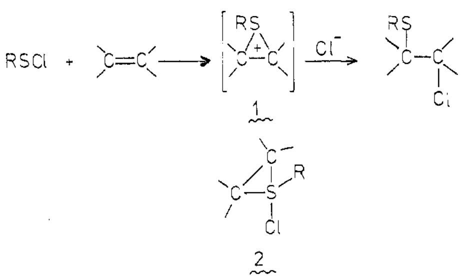
Electrophilic addition to a carbon–carbon double bond is one of the basic reactions in organic chemistry. The most widely accepted mechanism for Ad_E reactions, advanced in 1937,[1] involves the cyclic "onium ion" intermediate. Probably no other reaction mechanism has been popularized to such extent[2–5] and, at the same time, received so little direct experimental proof. The main reason is that the "onium ion" mechanism had served and continues to serve as a very convenient phenomenological basis for the understanding of the stereochemical course of many reactions.

Certainly at present there exist a variety of modern modifications of this mechanism, involving such intermediates as π complexes, nonclassical and classical ions, ion pairs, and polyvalent species.[2–7] However, all of them have two features in common: (a) the development of partial positive charge(s) on carbon atoms(s) is accepted; (b) different types of "bridging" are suggested for the explanation of the stereochemical results (strong "bridging" for trans addition and nearly "zero bridging"—as in an open carbenium ion—for the nonstereospecific additions).

The Ad_E reaction of sulfenyl chlorides appears to be one of the most efficient ways to transform alkenes into synthetically useful products, and it has been extensively studied and reviewed.[2–5,7–12] The classical mechanistic description of this process suggests rate-determining formation of an episulfonium ion (ESI, 1) which undergoes a nucleophilic opening by chloride anion at the second step[12] (Scheme I).

Scheme I



The uniformity and the simplicity of the steric course of this reaction (vide infra) are supposed to constitute—in accordance with traditional ideology of Ad_E mechanisms—convincing evidence in favor of this interpretation. Alternative suggestions about the involvement of other bridged species, such as covalent σ-sulfurane **2**, have also been advanced.[13] But since conclusive evidence for this point has been lacking, such an approach has never attracted any serious attention, and even recent articles and reviews on the subject give

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(1) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

(2) F. Freeman, *Chem. Rev.*, **75**, 439 (1975); R. D. Bach and H. F. Henneike, *J. Am. Chem. Soc.*, **92**, 5589 (1970).

(3) M. Jaszunski and E. Kochanski, *J. Am. Chem. Soc.*, **98**, 4624 (1977); K. Yates, in "Application of MO Theory in Organic Chemistry", Vol. 2, I. G. Csizmadia, Ed., Elsevier, Amsterdam, 1977, p 261.

(4) R. S. Fahey, *Top. Stereochem.*, **3**, 237 (1968); P. B. D. de La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam, 1966.

(5) G. H. Schmid and D. Garratt in "The Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley, New York, 1977, Chapter 9.

(6) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18, C71 (1951).

(7) W. A. Smit, *Zh. Vsesousn. Mendeleev Obshch.*, **22**, 300 (1977).

(8) N. Kharasch, "Organic Sulfur Compounds", Vol. 1, Pergamon, New York, 1961, p 375; W. H. Müller, *Angew. Chem.*, 81, 475 (1969); E. Kühle, *Synthesis*, 561 (1970); 563 (1971).

(9) P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, **43**, 1208 (1976).

(10) G. H. Schmid, C. L. Dean, and D. Garratt, *Can. J. Chem.*, **54**, 1253 (1976).

(11) L. P. Rasteikene, D. I. Greichute, M. G. Lin'kova, and I. L. Knunyantz, *Usp. Khim.*, **46**, 1041 (1977).

(12) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949); N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953); D. R. Hogg and N. Kharasch, *ibid.*, **78**, 2728 (1956).

(13) G. H. Helmkamp, D. Owsley, W. M. Barness, and H. N. Cassey, *J. Am. Chem. Soc.*, **90**, 1635 (1968); D. Owsley, G. H. Helmkamp, and S. N. Spurlock, *ibid.*, **91**, 3606 (1969); D. Owsley, G. H. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); see also V. Calo, G. Scorrana, and G. Modena, *J. Org. Chem.*, **34**, 2020 (1969).

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Chart I

MYTH: episulfonium ions	REALITY: episulfonium ions
1. are weak electrophiles having little positive charge on the carbon atoms	1. are active electrophiles of the bridged carbenium ion type
2. do not undergo skeletal rearrangements	2. are able to undergo skeletal rearrangements
3. should be regarded as "strongly bridged" species	3. are bridged species capable of interconversion and nonstereospecific reactivity
4. give *anti*-Markownikoff adducts as kinetically controlled products	4. react with nucleophiles giving preferentially Markownikoff adducts
5. are intermediates in the addition reactions of RSCl to olefins under typical conditions	5. are certainly not involved in the addition of RSCl to olefins under the usually accepted conditions

full credit to the episulfonium mechanism,[5,10,11,14] as was the case 30 years ago. At present *the ESI mechanism is universally used for the discussion of the addition reaction of sulfenyl chlorides to olefins.*[15]

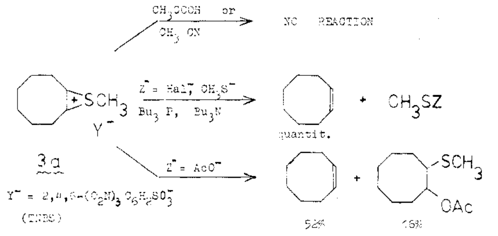
However, recent investigations in this area have led to quite unexpected and intriguing results which disclosed severe inconsistencies of the whole concept and necessitated its critical reappraisal. The aim of the present Account is to discuss these new data and their meaning for the understanding of the general mechanistic problems of RSCl addition to alkenes.

Addition of RSCl to Olefins and the Episulfonium Ion Myth

Evidence for the ESI mechanism was considered to be provided by (a) stereochemical results and (b) kinetic investigations. Thus it was found that the addition of RSCl proceeds almost universally as a trans stereospecific process.[16–20] Numerous data on the rates of reaction for various alkenes have shown that its kinetics obey a second-order rate law, in agreement with an Ad_E2 mechanism involving the formation of ion 1 as the first step (Scheme I).[4,5,10,21] This scheme, aside from being appealingly simple and useful, has been supported also by solvolysis data which suggest the participation of the sulfur atom of sulfides in stabilizing corresponding β-carbocations.[22]

At the same time a critical analysis of existing experimental data reveals rather serious discrepancies between the regularities of RSCl Ad_E reactions and generally held views about the reactivity patterns of cationoid intermediates. Thus it is assumed[2,4] that the formation of cationoid intermediates in any organic reaction (including the Ad_E process) reveals itself in the production of more or less complicated mixtures, due to the intrinsic ability of these intermediates to be involved in rearrangements, stereoconversions, and reactions with other nucleophiles present. None of these complications are typical for Ad_E reactions of RSCl. We list the following well-known features of this process[4,5,17] which appear especially strange in the light of the aforementioned concept:

Scheme II



(1) The formation of mixed adducts corresponding to the incorporation of external nucleophiles has not been usually observed, and even such nucleophilic solvents as CH_3COOH or CH_3CN can be used as reaction media.

(2) Skeletal rearrangements have been observed only in extremely rare cases.[4,23] Even *tert*-butylethylene,[5] norbornene,[24] or benzvalene,[25] all especially liable to undergo rearrangement, have been shown to yield unrearranged 1,2-adducts.

(3) The well-documented trans stereospecificity of RSCl addition was found to be insensitive to changes in the nature of the alkene and the reactants and to variations in the reaction conditions, all in striking contrast to the variability of the steric course of the majority of Ad_E processes.[2,4,26]

(4) Addition to unsymmetrical alkyl olefins proceeds abnormally and produces predominantly anti-Markownikoff adducts.[4,10,27]

In order to account for these peculiarities of the RSCl addition in terms of the traditional "onium" mechanism it was postualted that ESIs are especially strongly bridged species with little, if any, positive charge localized at the carbon atoms. For this reason they are not liable to participate in the reactions typical of other cationoid species, and the regioselectivity of their

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[14] W. S. Allison, *Acc. Chem. Res.*, **9**, 293 (1976).

[15] Moreover the latter reaction is often referred to as the reliable model of an onium ion-like process; see, for example, G. H. Schmid and T. T. Tidwell, *J. Org. Chem.*, **43**, 460 (1978).

[16] G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).

[17] V. R. Kartashov, I. V. Bodrikov, E. V. Scorobogatova, and N. S. Zefirov, *Phosphorus Sulfur*, **3**, 213 (1977); *Zh. Org. Khim.*, **12**, 297 (1976), and references therein.

[18] The nonstereospecific addition to *cis*-anethole was described by G. H. Schmid and V. J. Nowlan, *J. Org. Chem.*, **37**, 3086 (1972); *Can. J. Chem.*, **54**, 695 (1976); see also the discussion in ref 19 and 20.

[19] G. Mehta and P. N. Pandey, *Tetrahedron Lett.*, 3567 (1975); N. S. Zefirov, N. K. Sadovaja, V. N. Kirin, A. S. Koz'min, and I. V. Bodrikov, *Zh. Org. Khim.*, **13**, 229 (1977); N. S. Zefirov, V. N. Kirin, K. A. Potechin, A. S. Kozmin, N. K. Sadovaja, E. N. Kurkutova, and I. V. Bodrikov, *ibid.*, **14**, 1224 (1978).

[20] (a) T. C. Morrill and N. D. Saraceno, *Int. Congr. Pure Appl. Chem., 23rd, Boston*, Thesis, (1971); (b) N. S. Zefirov, N. K. Sadovaja, R. Sh. Achmedova, and I. V. Bodrikov, *Zh. Org. Khim.*, **14**, 662 (1978); (c) G. H. Schmid, D. Garratt, N. S. Zefirov, N. K. Sadovaja, R. Sh. Achmedova, I. V. Bodrikov, T. C. Morrill, and N. D. Saraceno, *Can. J. Chem.*, submitted for publication.

[21] C. L. Wilhins and T. W. Regulski, *J. Am. Chem. Soc.*, **94**, 6016 (1972).

[22] R. Bird, C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1221 (1973); E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978, Chapter 4.

[23] (a) S. Cristol and B. B. Jarvis, *J. Am. Chem. Soc.*, **88**, 3091 (1966); M. S. Raach, *J. Org. Chem.*, **40**, 161 (1975); (b) N. S. Zefirov, I. V. Bodrikov, N. K. Sadovaja, V. N. Moleva, and A. M. Maggerramov, *Zh. Org. Khim.*, **12**, 2474 (1976).

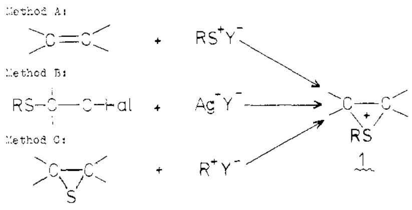
[24] H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5678 (1956).

[25] T. J. Katz and K. C. Nicolaou, *ibid.*, **96**, 1948 (1974).

[26] (a) NOCl: P. P. Kadzjauskas and N. S. Zefirov, *Usp. Khim.*, **37**, 1243 (1968); (b) HgX_2: N. S. Zefirov, *ibid.*, **34**, 1272 (1965).

[27] W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2075 (1968).

Scheme III



opening under the action of an internal nucleophile (Cl-) is not subject to charge control but is affected principally by steric hindrance[28] and/or by the specific electron density in LUMO[29] (see Chart I, left side).

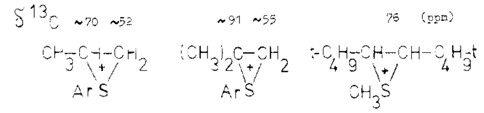
These considerations allow one to save the simplicity of the conventional description of the mechanism of RSCl addition. However, the postulated properties of ESIs appeared to be rather exceptional in comparison with those of other bridged onium species.[30] Hence the validity of the whole concept of the mechanism of the RSCl addition depended crucially on the adequacy of this artificially created image of ESI, and it was certainly a challenge to check the reasoning shown above by direct experiments.

Recent Developments in the Field

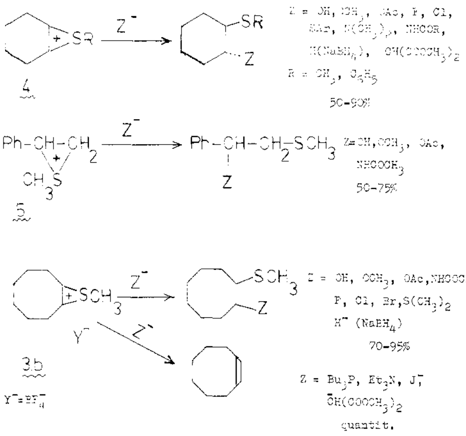
Although there have been several claims about the preparation of the stable episulfonium salts,[31] the first reliable data on their identification and properties were published by G. Helmkamp and co-workers[13] (Scheme II). It has been claimed that the reaction of salt **3a** with a variety of nucleophiles occurs with attack at the sulfur rather than on the carbon atom and that the corresponding 1,2-disubstituted cyclooctanes are formed only to a minor extent. The failure of CH_3COOH and CH_3CN to react with salt **3a** appeared to be especially significant in view of the known property of these solvents not to participate as nucleophiles in RSCl additions to alkenes. In general these results seemed to provide direct experimental support to the aforementioned suggestions about the poorly electrophilic nature of ESIs. However, further studies (vide infra) have shown that the experimental data on reactivity of **3** are only partially correct and that the general conclusions given in ref 13 are actually misleading.

Our investigations in the field started at the beginning of this decade. The initial work of Smit's group was concerned with the generation and chemical reactivity of episulfonium ions.[32-34] In sharp contrast to the generally accepted opinion, it was shown that *episulfonium ions reveal the normal electrophilic properties of cationoid species*. At the same time, the efforts of Zefirov's and Bodrikov's groups were aimed at the problems of increasing the effective electrophilicity of sulfenyl chlorides. In these initial studies[17,35,36] it was disclosed that the course of RSCl Ad_E reactions could be dramatically altered and that *the reactions could be made to yield products typically formed in carbenium ion like processes.*

Scheme IV



Scheme V



These data evidently contradict the accepted view discussed earlier, and they made us intuitively feel that more adequate understanding of the whole problem was coming.

Experimental Evidence on the Properties of Episulfonium Ions

At present several methods are available for the preparation of ESIs (Scheme III). Methods A and B seem to be of general utility[34,37] (vide infra). The successful use of method C was reported only for the preparation of *S*-methyl-ESI from *cis*-di-*tert*-butylethylene[38] and for the series of *S*-alkyl-ESIs from cyclooctene.[13] The essential feature of all these procedures is the use of nonnucleophilic counterions such as BF_4^-, PF_6^-, SbF_6^-, $SbCl_6^-$, TNBS-, or FSO_3^-. As a rule the formation of ESIs proceeds quite smoothly in usual organic solvents (e.g., CH_2Cl_2–$C_2H_4Cl_2$ or CH_3NO_2). In most cases the prepared ESIs were found to be unstable at elevated temperatures, and only a few reports describe their isolation as pure substances.[37,38] The stability of the solutions of ESIs (evaluated by NMR data and/or by the yields of quenching adducts) varies from several hours at -70 °C up to several days at ambient temperatures.[34,39]

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(28) W. A Thaler, W. H. Mueller, and P. E. Butler, *ibid.*, **90**, 2069 (1968).

(29) Y. Kikuzono, T. Yamabe, S. Nagata, H. Kato, and K. Fukui, *Tetrahedron*, **30**, 2197 (1974).

(30) G. A Olah, "Halonium Ions", Wiley-Interscience, New York, 1977.

(31) L. Goodman, A. Benitez, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 1680 (1958); P. P. Budnikoff and A. E. Shilov, *Ber.*, **55B**, 3848 (1922); O. V. Kildisheva, M. G. Linkova, L. P. Rasteikene, V. A. Zabelaite, N. K. Potsute, and I. L. Knunjantz, *Dokl. Akad. Nauk SSSR*, **203**, 1072 (1972).

(32) W. A. Smit, A. V. Semenovsky, O. V. Lubinskaya, T. N. Chernova, M. Z. Krimer, and V. F. Kucherov, *Tetrahedron Lett.*, 3101 (1971).

(33) M. Z. Krimer, W. A. Smit, and A. A. Shamshurin, *Dokl. Akad. Nauk SSSR*, **208**, 864 (1973).

(34) W. A. Smit, M. Z. Krimer, and E. A. Vorobeva, *Tetrahedron Lett.*, 2451 (1975).

(35) (a) I. V. Bodrikov, L. G. Gurvich, N. S. Zefirov, V. R. Kartashov, and A. L. Kurtz, *Zh. Org. Khim.*, **10**, 1545 (1974); (b) N. S. Zefirov, N. K. Sadovaja, A. M. Maggerramov, I. V. Bodrikov, and V. R. Kartashov, *ibid.*, **10**, 2620 (1974).

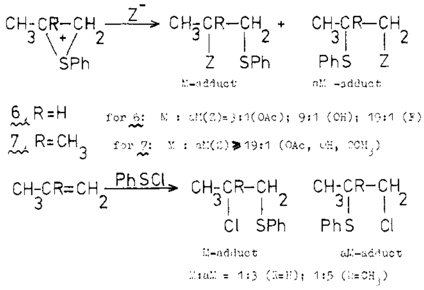
(36) (a) N. S. Zefirov, N. K. Sadovaja, A. M. Magerramov, I. V. Bodrikov, and V. E. Kartashov, *Tetrahedron*, **31**, 2948 (1975); (b) N. S. Zefirov, N. K. Sadovaja, L. A. Novgorodtseva, and I. V. Bodrikov, *Zh. Org. Khim.*, 14, 1806 (1978).

(37) G. Capozzi, O. De Lucchi, V. Luccini, and G. Modena, *Tetrahedron Lett.*, 2603 (1975).

(38) P. Raynolds, S. Zonnebelt, S. Bakker, and R. M. Kellogg, *J. Am. Chem. Soc.*, **96**, 3146 (1974).

(39) (a) W. A. Smit, A. S. Gybin, V. S. Bogdanov, M. Z. Krimer, and E. A. Vorobieva, *Tetrahedron Lett.*, 1085 (1978); (b) A. S. Gybin, W. A. Smit, M. Z. Krimer, E. A. Vorobieva, and V. S. Bogdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 510 (1978); (c) A. S. Gybin, W. A. Smit, M. Z. Krimer, and V. S. Bogdanov, *ibid.*, 2156 (1978); (d) A. S. Gybin, M. Z. Krimer, W. A. Smit, N. S. Zefirov, L. U. Novgorodtseva, and N. K. Sadovaja, *Zh. Org. Khim.*, **15**, 1361 (1979).

Scheme VI



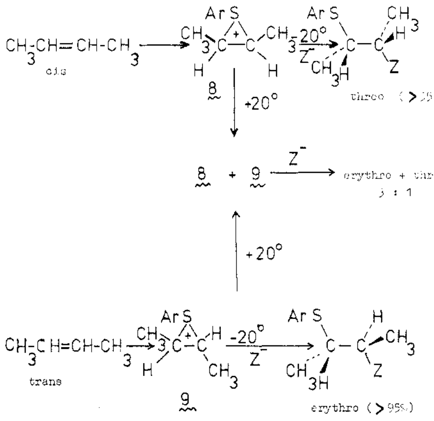
Typical values of chemical shifts in ^{13}C NMR spectra of ESIs are shown in Scheme IV. The comparison of these data with those for uncharged thiiranes disclosed that $\Delta\delta$ for bridged carbon-13 atoms varies from 25 to 30 ppm.[38,39a] These values are rather close to those reported for pairs of acyclic sulfonium salts and sulfides.[38] The existing NMR data *do not contradict* the suggestion of the comparatively low localization of positive charge on the carbon atoms.

At present extensive experimental data[32-34,38-41] show that, contrary to expectations, the most usual result of ESI reactions with various nucleophiles is the formation of the corresponding 1,2-adducts arising from predominant (if not exclusive) C attack by the nucleophile. This reactivity pattern was demonstrated for ESIs derived from acyclic or cyclic alkenes as well as from aryl olefins, and typical examples are given in Scheme V. In particular it has been disclosed[42] that ESI **3b** (Y = BF_4) undergoes "normal" C attack by a variety of nucleophiles, including those previously reported[13] to be inert toward **3a** or to attack the latter exclusively on the sulfur atom (compare Schemes II and V).

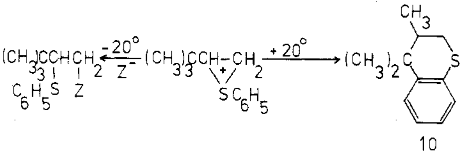
The relative ease of the quenching reactions of ESIs with various nucleophiles (thus the reactions in Scheme V are usually complete within minutes at −20 to 0 °C) clearly demonstrates that ESIs reveal the reactivity patterns quite typical of cationoid electrophiles, e.g., cyclic halonium ions.[30] Thus, direct experimental data unambiguously prove that the *existing speculative suggestions about the weakly electrophilic nature of ESIs are incorrect and must be abandoned.*

The outcome of the reactions of ESIs derived from unsymmetrical alkenes under the action of various nucleophiles is demonstrated in Scheme VI, along with selected data on the regioselectivity of RSCl addition to the respective alkenes.[5,10] These data show that the opening of an ESI leads to the predominant or exclusive formation of Markownikoff adducts.[39a-c] Hence the *generally held assumption about the intrinsic tendency of ESI to produce abnormal anti-Markownikoff adducts is wrong*, and the data on the anti-Markownikoff regioselectivity of RSCl addition to alkenes (e.g., as in Scheme VI) must actually be taken as evidence against the involvement of ESIs in the latter process.

Scheme VII



Scheme VIII



The experimental data on the steric course of the ring opening of ESIs derived from stereoisomeric 2-butenes (Scheme VII) disclose that this process is highly stereospecific and exclusively affords erythro adducts from the *trans*-alkenes and threo adducts from the *cis*-alkenes. This stereochemistry was found to be insensitive to changes in the nature of S-aryl substituent or to variation of nucleophiles used in quenching[34,41] (cf. ref 16).

However, we have also found that the net result of the transformation alkene → adduct could be dramatically affected by a change of experimental conditions. Thus if a solution of **8** or **9** (prepared as usual at −50 °C) is warmed up and kept for several hours at ambient temperature, then the subsequent quenching of the mixture with CH_3COOH yields a mixture of both erythro and threo acetates, with their ratio (1:3) being independent of the stereochemistry of the starting ESI (Scheme VII).[41] These data point out that ESIs, which are configurationally stable at low temperatures, are capable of undergoing stereoconversion upon being moderately heated. Hence the generally held belief[16] that the episulfonium ion bridge *is exceptionally stable and can withstand elevated temperatures (up to 140 °C) without any noticeable tendency to rotate freely must be considered as erroneous.*

The observed stereoconversion of isomeric ESIs (Scheme VII) must necessarily proceed via an open carbenium ion. Hence one could have expected that under similar conditions ESIs would also be able to undergo carbenium ion reactions of other types—namely skeletal rearrangements. To verify this suggestion we have studied the behavior of ESIs derived from *tert*-butylethylene.[40c] It was disclosed that these ESIs are quite stable at −50 to −20 °C and afford the usual 1,2-adducts upon quenching. However, if the solution of *S*-phenyl-ESI is warmed up to +20 °C a rearrangement occurs resulting in the exclusive formation of the product **10** (Scheme VIII), corresponding to a 1,2-methyl shift in the ESI with the subsequent intramolecular electrophilic aromatic alkylation of the *S*-aryl moiety. These results[40c] *clearly demonstrate*

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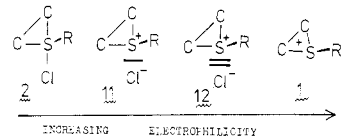
(40) E. A. Vorobieva, M. Z. Krimer and W. A. Smit, *Izv. Akad. Nauk SSSR, Ser. Khim.*: (a) 2832 (1974); (b) 125 (1975); (c) 1318 (1976).

(41) E. A. Vorobieva, M. Z. Krimer, and W. A. Smit, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2743 (1976).

(42) A. S. Gybin, W. A. Smit, M. Z. Krimer, N. S. Zefirov, N. K. Sadovaya, L. A. Novgorodtseva, and I. V. Bodrikov, *Tetrahedron*, in press. The use of **3b** instead of **3a** in this study was dictated by better solubility properties of the former in most organic solvents. Control experiments have shown that both salts **3a** and **3b** behave similarly toward such nucleophiles as acetate or hydride ion. The possible reasons for the discrepancy between the results of this study and earlier data[13] will be discussed in the full paper.

Scheme IX



that ESIs should in fact be regarded as "masked" carbenium ions and are able to react with rearrangement under properly chosen conditions.

The results discussed above provide convincing evidence that ESIs are able to take part in all the processes usually associated with the formation of cationoid intermediates. In other words, the chemical behavior of real ESIs has very little in common with the preconceived reactivity pattern generally associated with these species on purely speculative grounds (compare left and right parts of Chart I).

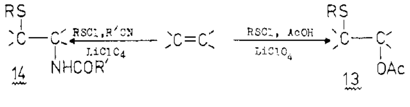
It is also worthwhile to emphasize that the preparation of an ESI via route A (Scheme III) and its subsequent quenching with a nucleophile can be regarded as an experimental model which provides a clear insight into the specific features of the reactions involving the formation of ESI as a real intermediate. The observed sharp differences in the course of this reaction compared with that of RSCl addition to alkenes[43] justify the following conclusion: *the peculiar features of RSCl addition to alkenes (see above) under usually adopted conditions should not be ascribed to the "strange nature" of ESIs but must be taken as an argument for the involvement of bridged intermediates less polar than ESIs.*

Course of RSCl Additions under Conditions of Increased Polarity

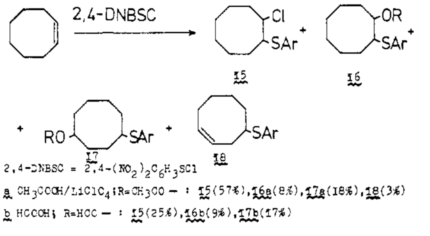
An alternative approach to the problem discussed here has been based on the assumption that *Ad_E reactions of RSCl could actually proceed via a number of bridged intermediates of varying polarity, their importance* being dependent on the reaction conditions.[17] In fact, ESI 1 and σ-sulfurane 2 represent the limiting cases of the structures, with complete dissociation vs. complete covalent bonding of the S–Cl bond, respectively (Scheme IX). Other structures with varying degrees of S–Cl bond dissociation, such as a tight ion pair, 11, or solvent-separated ion pair, 12, might also be taken into account. Bearing in mind that ESI 1 is certainly the most electrophilic species among those shown in Scheme IX, it is instructive to consider the following question: is it possible to increase the effective electrophilicity of RSCl by varying the reaction media? Actually, if ESIs were really involved as the intermediates in this reaction under generally adopted (usually nonpolar) conditions, then the answer should be "no". On the contrary, the answer could be "yes" if the latter process involves less polar intermediates, such as type 11 or 12.

We have been able to show that *the answer is definitely "yes", and the course of RSCl addition to alkenes can be substantially changed if the reaction is carried out in the presence of strong electrolytes* (usually perchlorate salts). Exploration of this "doping-addition" principle has led to important theoretical and synthetically useful results. Thus as mentioned above olefins usually react with RSCl in CH_3COOH with exclusive formation of chlorosulfides. However, the same reactions carried out in the presence of $LiClO_4$ lead to appreciable amounts of corresponding acetoxy adducts 13 (Scheme X).[17,36,44,45] This approach brought about the development of a convenient procedure for the preparation of β-thio amides 14 from olefins (Scheme X).[44] The reaction with isomeric stilbenes demonstrated the stereospecificity of this pathway since the two isomers produce the opposite stereoisomers of 1-arylthio-2-acetoxy-1,2-diphenylethane.[45]

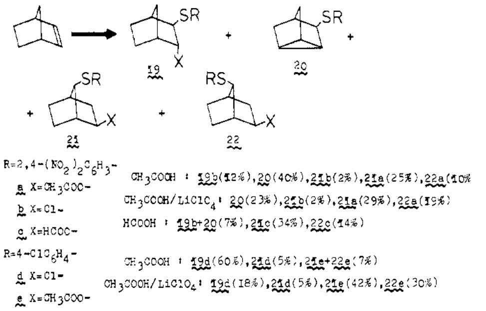
Scheme X



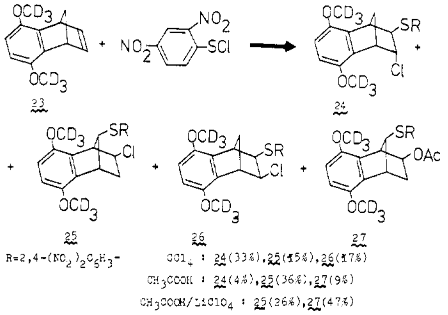
Scheme XI



Scheme XII



Scheme XIII



The addition of strong electrolytes can evidently sharply affect the polarity of the intermediate(s) as is evidenced by the unusual character of the RSCl addition to cyclooctene (Scheme XI).[46]

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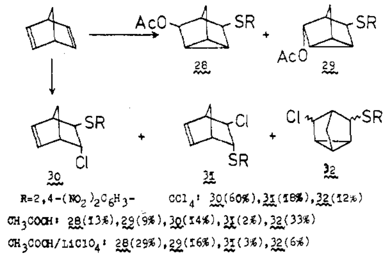
(43) It is necessary to emphasize that the experimental conditions of these two reactions are quite similar (solvents, temperature) and they differ only by the nature of sulfenyl electrophile.

(44) N. S. Zefirov, N. K. Sadovaya, A. M. Magerramov, and I. V. Bodrikov, *Zh. Org. Khim.*, 12, 903 (1976); 13, 245 (1977).

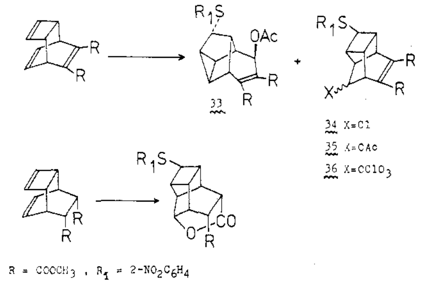
(45) N. S. Zefirov, N. K. Sadovaya, L. A. Novgorodtseva, and I. V. Bodrikov, *ibid.*, 14, 463 (1978).

(46) The exclusive formation of 15 is observed[45] for the reaction of cyclooctene with 2,4-DNBSC in CH_3COOH in the absence of $LiClO_4$ (yield 50%). The reaction of cyclooctene with ArS^+BF_4 (prepared in situ, Ar = 2,4-$(O_2N)_2C_6H_3$) in CH_2Cl_2–$C_2H_4Cl_2$ at –60 °C followed by the quenching with CH_3COOH produced the mixture of 16, 17, and 18 in the ratio 10:1:8.

Scheme XIV



Scheme XV



This method gave especially spectacular results for the reactions with strained olefins. Thus the addition of arylsulfenyl chloride to norbornene in the presence of $LiClO_4$ results in the formation as the main products of the rearranged syn and anti acetates, **21** and **22** (respectively)[36,47] (Scheme XII).

The addition of 2,4-dinitrobenzenesulfenyl chloride (2,4-DNBSC) to dimethoxybenzonorbornadiene (**23**) in AcOH results in the predominant formation of the rearranged chloride **25** (Scheme XIII), but in the presence of $LiClO_4$ the formation of the rearranged acetate **27** is the predominant pathway.[23b,48,49]

In the case of norbornadiene (Scheme XIV) the addition of RSCl in the presence of $LiClO_4$ proceeds with homoallylic participation of the second double bond and gives a mixture of the two nortricyclenic acetates **28** and **29**.[20b,c]

The unusual course of RSCl addition under such conditions allows one to perform some interesting transformations in a series of polycyclic olefins such as those shown in the Scheme XV.[50] It is noteworthy to emphasize that the formation of the stable perchlorate **36** is the first example of the participation of perchlorate ion as a nucleophile in the final step of an electrophilic addition.

We have also found that an effect similar to that arising from the presence of strong electrolytes could be observed for the RSCl addition carried out in solvents with high ionizing power. Thus the addition of 2,4-DNBSC to norbornene in HCOOH proceeds both with Wagner–Meerwein rearrangement and incorporation of solvent (Scheme XII).[48] The analogous reaction with cyclooctene produces noticeable amounts of a 1,4-product resulting from a 1,5-hydride shift (Scheme XI).[36b]

Substantial changes in the course of RSCl addition also have been observed for reactions carried out in liquid SO_2. In this solvent the facile Wagner–Meerwein rearrangement (e.g., **23** → **25**) as well as the preferential formation of Markownikoff adducts (e.g., for the reaction with isobutylene and trimethylethylene) as the kinetically controlled products have been observed.[20c,39d]

Summing up the results given in this section, we emphasize that *the observed "doping–addition" effect must be taken as clear-cut evidence (i) against the involvement of ESIs under usually adopted conditions of RSCl addition and (ii) in favor of the idea of the intermediate formation of ion pairs in these addition reactions.*

General Outline of the Mechanism of RSCl Addition

We believe that the main results of the studies presented are: (1) the identification of the mechanistic extremes in RSCl addition (via **1** and **2**), (2) the experimental evaluation of the reactivity pattern of the intermediate of one of these extremes, namely ESI (**1**), (3) the demonstration of the involvement of intermediates with various degrees of S–Cl bond dissociation, and (4) the possibility of governing the course of RSCl addition by the choice of proper reaction conditions.

In fact, the limiting case in the polar mechanism is evidently realized in the addition of cationoid reagents of the type RS^+Y^-. The peculiar features of this process (see above) could serve as a reliable diagnostic tool, allowing the detection of the possible participation of ESI-like intermediates under the various conditions of RSCl addition.

On the other hand, comparison of the data discussed earlier discloses specific features of the mechanism for the RSCl Ad_E reaction under typical nonpolar conditions. This reaction should most certainly involve the formation of bridged intermediates which, however, must be substantially less polar than the ESI. At present there is no direct experimental data enabling one to specify unambigously the structure of this intermediate. Nevertheless the covalent σ-sulfurane **2**[13] could be considered plausible, both in view of the numerous data on stable σ-sulfuranes of other structural types[51] and of recent ab initio calculations.[52] However, this ab initio calculation showed that the charge separation, S^+Cl^-, in this covalent intermediate is rather large, since the chlorine atom has assumed 75% of the full negative charge. Thus, the strict distinction between species of **2** and **11** may be questionable. The experimentally found occurrence of processes characterized with both features—(1) the presence of relatively large positive charge on carbon atoms as judged by the formation of rearranged products and (2) the absence of the complete dissociation of the S–Cl bond as judged by formation of rearranged chlorides, e.g., **25** (but not acetates!)—may be taken as the evidence of the in-

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(47) K. A. Potechin, E. N. Kurkutova, M. Yu. Antipin, Yu. T. Struchkov, A. M. Magerramov, N. K. Sadovaya, and N. S. Zefirov, *Zh. Org. Khim.*, **13**, 2093 (1977).

(48) N. S. Zefirov, N. K. Sadovaja, L. A. Novgorodtseva, and I. V. Bodrikov, *Tetrahedron*, **31**, 1373 (1978).

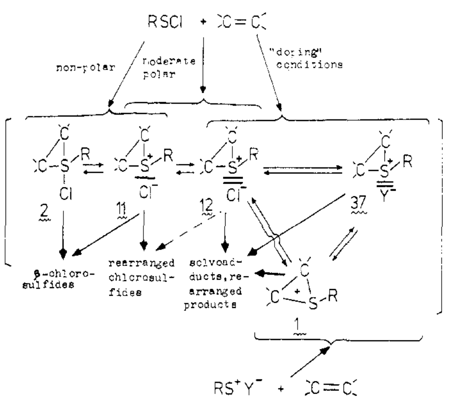
(49) The reaction of **23** with *o*-nitrobenzenesulfenyl chloride in CCl_4 yields 50% of trans chlorosulfide, 24% of rearranged chlorosulfide, and—rather unexpectedly—about 4% of *exo*-chloro-*endo*-arylthio adduct.

(50) (a) N. S. Zefirov, V. N. Kirin, A. S. Kozmin, I. V. Bodrikov, K. A. Potekhin, and E. N. Kurkutova, *Tetrahedron Lett.*, 2617 (1978); N. S. Zefirov, A. S. Kozmin, V. N. Kirin, V. V. Zhdankin, and I. V. Bodrikov, *Zh. Org. Khim.*, **14**, 2646 (1978). (b) The structure of acetate **33** has been determined by X-rays; the structures of **34**–**36** are supported by NMR.

(51) L. J. Adzima, E. N. Duesler, and J. C. Martin, *J. Org. Chem.*, **42**, 4001 (1977), and references cited therein.

(52) V. M. Csizmadia, G. H. Schmid, P. G. Mezey, and I. G. Csizmadia, *J. Chem. Soc., Perkin Trans. 2*, 1019 (1977); V. M. Csizmadia in "Application of MO Theory in Organic Chemistry", Vol. 2, I. G. Csizmadia, Ed., Elsevier, Amsterdam, 1977, p 280.

Scheme XVI



volvement of tight ion-pair intermediates **11**.

The balance between **2** and **11** as well as between **11** and **12** is rather delicate and should be subject to the effects of the medium and nature of the reagent. The addition of strong electrolytes can result in (i) the shift of an intermediate structure toward a more polar one (**2** → **11** or **11** → **12**) and (ii) the transformation of an ion pair **12** into other ion pairs (e.g., **37**) due to anion exchange in ion pairs. The formation of covalent perchlorates **36** (Scheme XV) seems to prove the importance of this process. The use of polar solvents (like HCOOH) or solvents capable of the specific solvation of Cl^- (like SO_2) appears to be especially favorable for the stabilization of solvent-separated ion pairs, and the net result of RSCl addition under these conditions can be very close to the reactions involving "bare" ESIs. This consideration allows the suggestion of a general mechanism for the reactions discussed covering the whole spectrum of polarity conditions (Scheme XVI).

The above considerations leave some aspects of the discussed mechanism unanswered. One of the most important of these is the problem of the possible pathways for the transformation of a σ-sulfurane or tight ion pair into an adduct with trans stereochemistry. This problem has been briefly discussed in the literature[17,36,52] but requires special theoretical analysis and additional experimental studies.

Conclusion

In conclusion, we wish to make several comments on the general methodology of organic mechanism investigations. In our opinion the creation of a concise mechanistic picture necessitates solving two basic problems: (i) experimental studies of the reactivity of the extreme alternative intermediates under conditions identical or sufficiently close to the real ones used in the reactions; (ii) elaboration of clear-cut experimental criteria which will allow in-between intermediate species to be identified. Thus, we are sure that the long discussed problem of the involvement of such cyclic intermediates as halonium[3,4] or mercurinium[4,26b] ions in Ad_E processes cannot be unequivocally solved without direct experimental studies of the reactivity of these species. At the present time such an approach is viable, and we believe that in this paper its fruitfulness has been demonstrated both for the analysis of mechanistic problems and for the extension of the synthetic utility of Ad_E reactions.

We express our sincere gratitude to Drs. E. P. Serebrjakov, O. S. Chizov, and Professor R. Caple for their helpful and encouraging discussions.

The 1,2 Hydrogen Shift: A Common Vehicle for the Disappearance of Evanescent Molecular Species

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Chemistry is intellectually challenging because it is constantly changing. One of the most pervasive examples of this metamorphosis is the manner in which "highly unstable intermediates" have a way of becoming rather well-characterized chemical species. One such example is trimethylenemethane, $C(CH_2)_3$. For many years considered a figment of the theorist's imagination,[1] trimethylenemethane is now becoming the focus of a number of experimental studies,[2] which have established conclusively[3] the triplet nature of the electronic ground state. More generally the entire classes of carbenes,[4-7] nitrenes,[8] and vinylidenes[9] have in recent years come to the forefront of chemical research.

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(5) W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, 1971.

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(8) W. Lwowski, "Nitrenes", Interscience, New York, 1970.

(9) P. J. Stang, *Chem. Rev.*, **78**, 383 (1978).

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