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# Polyhalovinyl Sulfones as Polyfunctional Electrophilic Substrates in Reactions with Nucleophiles

Bagrat A. Shainyan[a]
[a] Irkutsk Institute of Organic Chemistry, Irkutsk, Russia

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# POLYHALOVINYL SULFONES AS POLYFUNCTIONAL ELECTROPHILIC SUBSTRATES IN REACTIONS WITH NUCLEOPHILES

BAGRAT A. SHAINYAN
*Irkutsk Institute of Organic Chemistry, RUS-664033, Irkutsk, Russia*

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In the present review the results of investigations of the chemical properties of polyhalovinyl sulfones are summarized. The main accent is made on their ability to react with nucleophiles at different electrophilic sites depending on the nature and the number of halogen substituents as well as on the nucleophile. Special attention is given to the halophilic reduction of these electrophiles by soft nucleophiles. The synthetic potential of polyhalovinyl sulfones as synthons for various heterocycles in reactions with polydentate S- and N-nucleophiles is also demonstrated.

*Key words:* Polyhalovinyl sulfones, nucleophilic vinylic substitution, halophilic reduction, rearrangements.

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## 1. INTRODUCTION

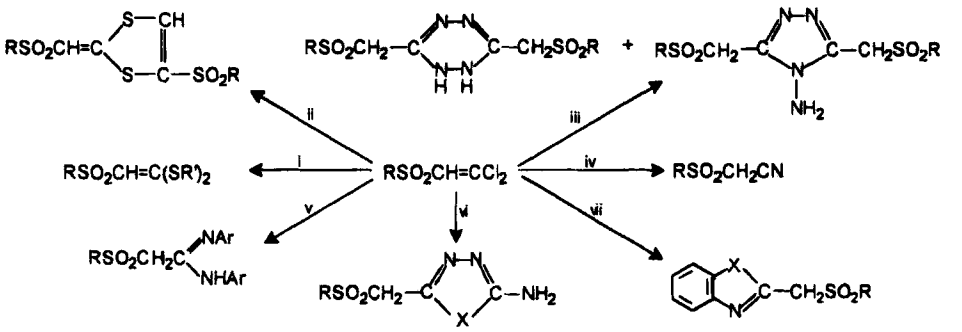
As early as the late 1950's β-halovinyl sulfones $RSO_2CH{=}CHX$ and α,β-dihalovinyl sulfones $RSO_2CX{=}CHX$ were among the first models used for the investigation of nucleophilic vinylic substitution reactions.[1-7] Possessing a sulfonyl group as a strongly activating acceptor group and a good leaving group they turned out to be convenient substrates for both preparative and kinetic studies in reactions with various nucleophiles and were therefore thoroughly investigated. However, the only process observed even with α,β-dihalovinyl sulfones in these early studies was that of substitution of the halogen

atom in the β-position. Our interest in polyhalovinyl sulfones of the common formula $RSO_2CX{=}CYZ$, with two or three halogen substituents, stemmed from their potential ability to react with nucleophiles at six electrophilic centers: $C_\alpha$, $C_\beta$, $H_\alpha$, $H_\beta$, $Hal_\alpha$, and, probably, $Hal_\beta$. It has been shown in our systematic studies of the reactivity of these compounds that all these possibilities can be realized depending on the nature of the substrate, the nucleophile, the leaving group, and the solvent. In many cases concurrent or consecutive reactions or both occur resulting in complicated product mixtures. The crucial role of the halogen has been demonstrated by comparison of the behavior of fluoro-, chloro-, bromo-, and iodovinyl sulfones containing different halogens in different combinations.

This Account discusses the main trends governing the reactivity of polyhalovinyl sulfones the main goal not being to present a comprehensive review, but rather to demonstrate their rich synthetic potential as well as a wide variety of mechanistic variations they can exhibit depending on the nature of the halogens, the nucleophile, the solvent, etc.

## 2. $C_\beta$ ATTACK

Under the influence of the acceptor group $RSO_2$, the C=C bond of dihalovinyl sulfones is polarized in such a way that the terminal $C_\beta$ atom becomes more electrophilic than the $C_\alpha$ atom and thus $C_\beta$ attack is the preferred route for both α,β- and β,β-dihalovinyl as well as for trihalovinyl sulfones. This mechanism is operative in reactions of $RSO_2CH{=}CCl_2$ with thiolates,[8,9] xanthates,[10] ammonia,[11] phenols,[12] simple and functionally substituted anilines,[12-14] hydrazine[15,16] and alkylhydrazines,[17] as well as semicarbazide and thiosemicarbazide[18]; in reactions of $RSO_2CH{=}CBr_2$ with thiolates,[19] in those of $RSO_2CX{=}CHY$ (when only Y is displaced) with alkoxides and thiolates;[6-7,20] and, probably, in the first stages of the reaction of $RSO_2CF{=}CFBr$ with thiolates.[21] Due to the presence of two geminal leaving groups in β,β-dihalovinyl sulfones, this $C_\beta$ attack allows various types of heterocycles to be obtained in reactions with polydentate nucleophiles. Some representative examples are shown in Scheme 1 which suggests participation of either one or two molecules of the substrate in these intra- or intermolecular heterocyclizations, respectively.




i: R'SNa; ii: $Na_2S$ or ROC(S)SNa; iii: $N_2H_4$; iv: $NH_3$; v: $ArNH_2$; vi: $H_2NC(O)NHNH_2$ (X = O, S); vii: o-$H_2NC_6H_4XH$ (X = O, S, NH)

SCHEME 1

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Mechanistically, a $C_\beta$ attack represents the first step of the carbanionic mechanism of nucleophilic vinylic substitution discussed in great detail in several reviews.[22] Although the most typical fate of the intermediate carbanion (or a zwitterion in case of neutral nucleophiles) is loss of a leaving group, some other possibilities exist as well and are to be discussed below.

It is noteworthy that polyhalovinyl sulfones bearing different halogens at the $C_\beta$ atom (like $RSO_2CH{=}CFBr$ or $RSO_2CF{=}CFBr$) are convenient models for the investigation of the intramolecular element effect (IEE) in nucleophilic vinylic substitution, i.e. the competitive substitution of F and X in a geminal C=CFX moiety (see[23] and references cited therein).

## 3. $H_\alpha$ ATTACK

The $H_\alpha$ attack is the first step of the elimination-addition mechanism of nucleophilic vinylic substitution with the formation of an acetylenic intermediate. This route is followed when β,β-dihalovinyl sulfones react with strong bases like alkoxides, especially in the first step where the halogen atom *trans* to the $H_\alpha$ atom is substituted.[19,24] Judging from the structure of the products it is impossible to distinguish between the elimination-addition and the carbanionic mechanism:

$$\underset{\mathbf{1}}{RSO_2CH{=}CX_2} \xrightarrow{R'O^-} RSO_2CH{=}C(OR')_2 \xrightarrow{H_2O} \underset{\mathbf{2}}{RSO_2CH_2COOR'} \qquad (1)$$

The most reliable criteria of this mechanism are proton exchange in a deuterated solvent and the sign of the entropy of activation. Thus, it has been shown that the starting material recovered from reaction (1) in R′OD is α-deuterated, and that the entropy of activation is positive.[19,24,25] On the other hand, reactions of $RSO_2CH{=}CX_2$ with soft nucleophiles such as $ArS^-$ are characterized by negative $\Delta S\neq$ and are not accompanied by proton exchange.[8,26] Apparently, the elimination-addition route and the carbanionic mechanism may both contribute to the total process, in particular in the second step of the reactions with alkoxides.[19,24]

The changes in the rates of substitution upon α-methylation are strongly different for the $Ad_N$-E and E-$Ad_N$ mechanisms and may be used as a sensitive probe of the mechanism. This can be exemplified by comparing α-methyl β-chloro or β,β-dichlorovinyl sulfones vs. the α-H ones in reactions with soft and hard nucleophiles.[22a,26,27] The retardation by two orders of magnitude of the reactions with thiolates reflects mainly destabilization of the intermediate carbanion by the donor effect of the α-Me group. This effect is somewhat stronger for $MeO^-$ as the nucleophile ($10^3$) which suggests contribution of the E-$Ad_N$

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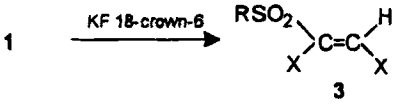
mechanism, and it reaches almost five orders of magnitude (70,000) in the reaction with sodium ethoxide.[26] As expected, in the reactions of all these α-methylated species the entropy of activation is negative.

The fate of the acetylenic intermediate $RSO_2C{\equiv}CX$ formed in the first stage depends on the solvent. While in alcohols the reaction is as given in eq. (1), in an aprotic nonpolar solvent (benzene) a hitherto unknown rearrangement of $RSO_2CH{=}CX_2$ to (*Z*)-$RSO_2CX{=}CHX$ occurs:[28,29]

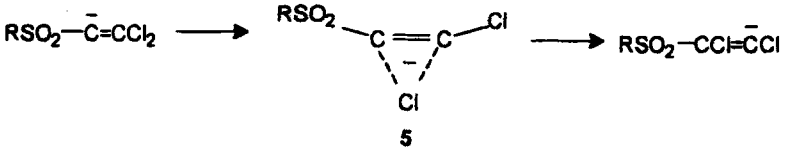



(2)

That the rearrangement is base-induced is proven by the fact that use of $R'O^-$ instead of KF in reaction (2) does not change the reaction course.[29] On the other hand, reactions with KF in aprotic dipolar solvents (DMSO, DMF) do not lead to the rearranged isomers, but follow the $C_\beta$ attack route and give the substitution-addition products $RSO_2CH_2CF_3$:[30]


(3)

The mechanism of rearrangement (2) has been studied[31–34] and its rate shown to be temperature-independent[32] which implies that the enthalpy of activation is close to zero and the entropy of activation negative. This is in accordance with an intramolecular mechanism of the rearrangement of the intermediate vinyl anion *via* a bridged transition state **5** rather than with an intermolecular mechanism *via* the acetylenic intermediate $RSO_2C{\equiv}CCl$. Although a 1,2-anionic rearrangement is formally forbidden by the rules of orbital symmetry it has been suggested that the contribution of the carbenoid structure [$RSO_2\bar{C}{=}CX_2 \leftrightarrow RSO_2\ddot{C}{-}\bar{C}X_2$] reduces the symmetry barrier to migration of X. If this is so, the rearrangement is a peculiarity of unsaturated carbanions because in saturated species a stabilization of this kind is impossible without breakage of the C−C bond.[31,34] An intermolecular mechanism, however, cannot be ruled out since it is favored energetically (at the MNDO level).[34] There are too many arguments for and against both paths to allow a conclusive answer concerning the mechanism of the rearrangement.

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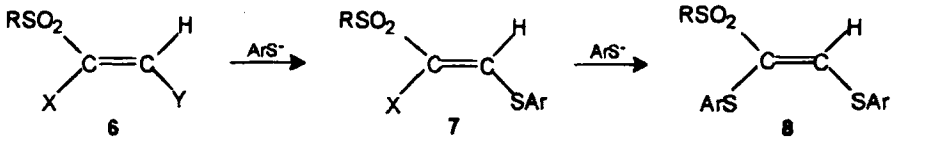
## 4. $C_\alpha$ ATTACK

The $C_\alpha$ attack is probably the most intriguing since in a series of earlier papers substitution of α,β-dihalovinyl sulfones was shown to lead to the substitution of only the halogen atom in the β-position.[1,5–7] However, later it was found that α,β-dihalovinyl sulfones react with sodium thiolates with substitution of both halogens, that in the β-position occurring first:[20,21]




6 7 8

X = F, Br, I; Y = Cl, Br, I; R = Ph (4)

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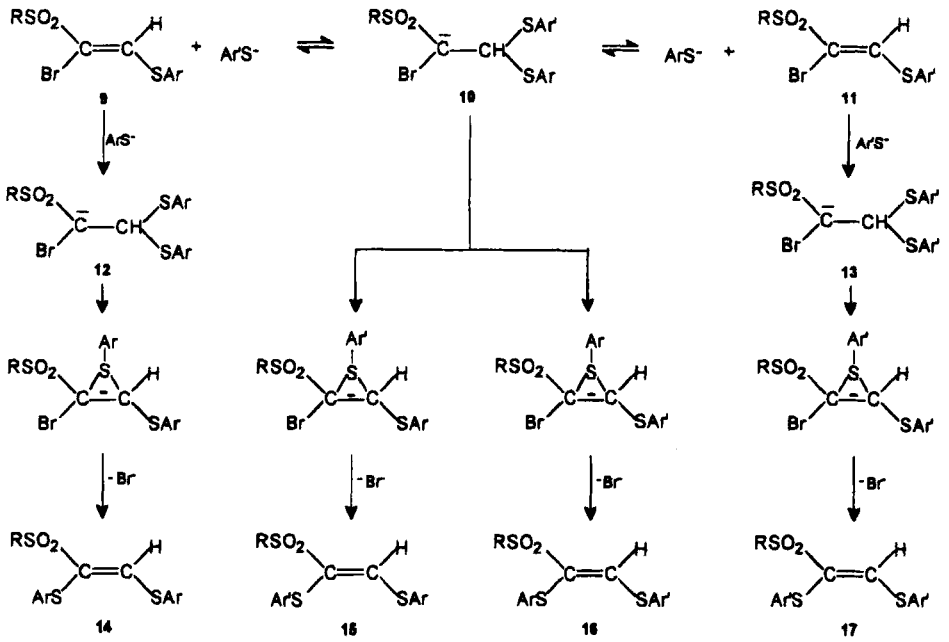
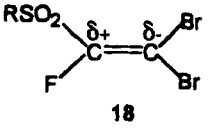
The conventional mechanism involving nucleophilic attack on the carbon bearing the leaving group (which, no doubt, is the case for substitution at the β-position) was questioned by us for substitution at the less activated α-position.[20] Recently special attention has been paid to this problem, and the mechanism shown in Scheme 2 has been suggested based on the results of cross-experiments and an analysis of a kinetic model of the process.[35]

Nearly the same **14**:**15**:**16**:**17** ratios of about 12:70:4:14 for the reaction of **9** (Ar = *p*-Tol) with *p*-$ClC_6H_4S^-$ and of **11** (Ar = *p*-$ClC_6H_4$) with *p*-$TolS^-$ were obtained which is in excellent agreement with the calculated ratio of 12:74:2:12 for Scheme 2.[35] It is noteworthy that the ArS/Ar'S exchange in the final products **14** and **17** takes place only at the β-position while no exchange occurred at the α-position. Therefore, the experimental data are in better agreement with a mechanism including 1,2-migration of the arylthio group than with a direct attack at the less activated α-carbon. The idea of a 1,2-migration of the nucleophilic group during vinylic substitution has also been proposed for some related processes to account for the formation of unusual products.[36–38] The possible preference of the intramolecular mechanism with 1,2-migration over the intermolecular direct $C_\alpha$ attack is probably due to an entropy effect similar to that responsible for the higher π-nucleophilicity.[39] Carbanions of the type $RSO_2C(SAr)(Br)\text{-}\overline{C}HSAr'$ formed after opening of the bridged anions, although obviously less stable than **10**, **12**, or **13**, have the lone pair on the β-carbon as an 'internal nucleophile' in close proximity to the $C_\alpha$ reaction center. This avoids entropy loss and also diminishes the energy barrier for the $Br^-$ expulsion owing to smaller changes in the interelectronic repulsion on going from **10**, **12**, or **13** to the corresponding transition states.[39]

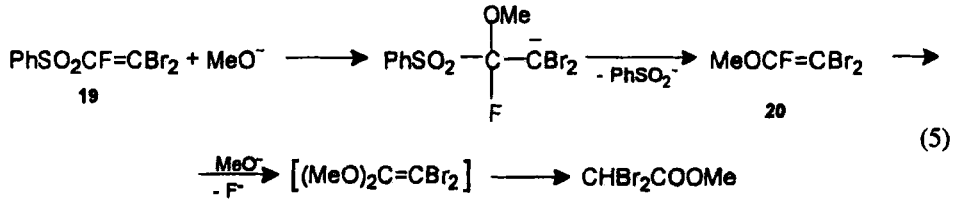


SCHEME 2

The most striking example of a $C_\alpha$ attack has been observed with the α-fluorinated sulfone $RSO_2CF{=}CBr_2$.[21] In its reaction with $MeO^-$ the best leaving groups, the bromine atoms, remain intact with all transformations occurring at the $C_\alpha$ reaction center. That the hard base ($MeO^-$) attacks the $C_\alpha$ atom *directly*, unlike in Scheme 2, may be explained by a combined action of the inductive and conjugative effects of the fluorine atom, which surpass the effect of the sulfonyl group and induce such a polarization of the C=C double bond that the $C_\alpha$ atom becomes the most electrophilic site in the substrate:



With this, the sulfonyl group wins in the competition with the fluorine as a leaving group in the intermediate carbanion:



(5)

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The intermediate methyl α-fluoro-β,β-dibromovinyl ether **20** has been isolated and its structure proven by $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra.[21,40] It is noteworthy that, as a rule, alkoxides do not react with halovinyl sulfones at the α-position (see Scheme 4 below).

With the α,β-difluoro-β-bromovinyl sulfone **21** no reaction at the α-position occurred with $MeO^-$; with a soft nucleophile ($p$-$ClC_6H_4S^-$) the α-fluorine atom is displaced but, like in eq. (4), only after the halogens in the β-position:[21]

$$\underset{\mathbf{21}}{PhSO_2CF{=}CFBr} + ArS^- \longrightarrow PhSO_2CF{=}C(SAr)_2 \xrightarrow{ArS^-} \underset{\mathbf{22}}{PhSO_2C(SAr){=}C(SAr)_2} \quad (6)$$

## 5. HALOPHILIC ATTACK

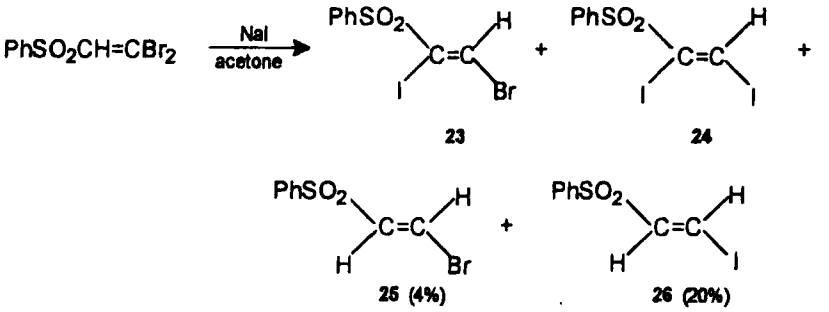
Although halophilic reactions are well known for haloacetylenes[41,42] as well as for saturated species,[43] there are rather few examples of such reactions in vinyl halides and, in particular, in polyhalovinyl sulfones.

To the best of my knowledge, in all known examples of halophilic reduction during nucleophilic vinylic substitution, it proceeds as a side reaction accompanying the main process of substitution at the β-position. Two points should be kept in mind to account for the structure of the reduction products: (i) the halogen atom in the α-position is more prone to nucleophilic attack, and (ii) the heavier the halogen is, the easier it is attacked by a nucleophile. This can be exemplified by the reactions of 2,3-dihalocrotononitriles[44] and ethyl 2,3-dihalocrotonates[45] with thiolates, with halophilic reduction occurring with the heavier halogen (Br) and only in the α-position [eq. (7)]:

$$M{-}CX{=}CX{-}Me \xrightarrow{RS^-} \begin{cases} M{-}C(SR){=}C(SR){-}Me & (X = Cl) \\ M{-}CH{=}C(SR){-}Me & (X = Br) \end{cases} \quad (7)$$

$M$ = CN, COOEt; X = Cl, Br

With dihalovinyl sulfones the reduction products are formed in the course of a new rearrangement under the action of iodide anions in acetone:[46]




(8)

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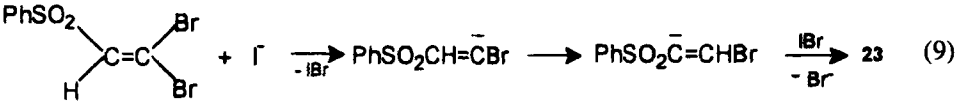
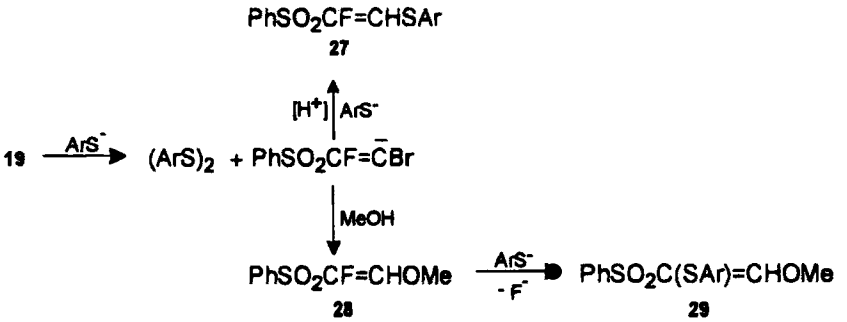
The rearrangement in eq. (8) is reminiscent of that in eq. (2) in that the major products are also α,β-dihalovinyl sulfones with Z-configuration. The similarity is, however, at best apparent. Iodide ion, contrary to fluoride ion, represents one of the softest nucleophiles and, as such, hardly attacks the $H_\alpha$ atom of the β,β-dihalovinyl sulfones **1** as the fluoride ion does. The rearrangement, probably, also proceeds *via* a vinyl anion which, however, is formed upon halophilic attack, like in eq. (9):



The possibility of vinyl anions to abstract a positive halogen in an oxidative manner is well documented in the literature.[47] There are two possible ways of formation of the reduced products **25** and **26**, that of nucleophilic attack of $I^-$ at the halogen in the β-position and its attack at the α-iodine atom of **23** or **24**. Since the configuration of the reduced products **25** and **26** coincides with that of the rearranged products **23** and **24**, an α-halophilic attack seems to be more likely, which is also in agreement with the tendency found in the literature.[44,45]

Sulfone **19** which behaves anomally in its reaction with $MeO^-$ [eq. (5)], undergoes preferential halophilic reduction with thiolates, unlike the trihalovinyl sulfone **21** [eq. (6)]:[21]



SCHEME 3

Not even traces of the product of complete substitution were found. Product **29** is the major one in the absence of excess ArSH. Use of excess ArSH surpasses the formation of the free methoxide ion and results in a preferential formation of **27**. Note that substitution at the α-position again proceeds only with soft nucleophiles.

## 6. $H_\beta$ ATTACK

I know of only one example of $H_\beta$ attack in halogenated vinyl sulfones, namely, that of (Z)-$PhSO_2CI{=}CHI$ in its reaction with sodium methoxide[20] affording methyl (phenylsulfonyl)-

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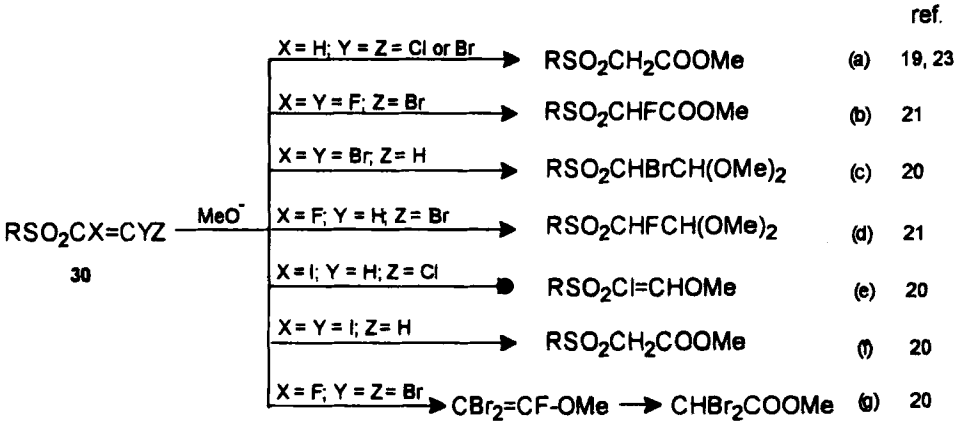
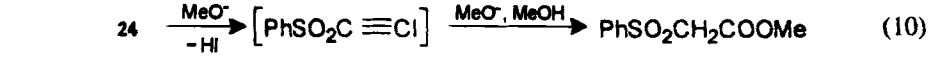
acetate $PhSO_2CH_2COOMe$. It was because of this unusual course of reaction that this compound was first erroneously assigned the structure of a β,β-diiodovinyl sulfone.[46]

As can be seen from Scheme 4, in reactions of all α-halogenated species with methoxide, the α-halogen atom remains intact (reactions b–e), with two exceptions (reactions f and g).




SCHEME 4

In reaction (g) the $C_\alpha$ attack takes place due to the reasons discussed above [see eq. (5)]. As to reaction (f), it has been shown by kinetic studies that the first iodine atom is displaced with a positive entropy of activation, which suggests an elimination-addition mechanism:




(10)

That the dehydrohalogenation takes place with only α,β-diiodovinyl sulfones and not with α,β-dibromo or α-iodo-β-chloro derivatives is probably due to the enhanced acidity of the vinyl proton in **24** (*e.g.*, $\Delta pK_a = pK_a$ (CHCl=CHCl) − $pK_a$ (CHI=CHI) is *ca.* 2 units[48]).

## 7. CONCLUSION

From the results presented in this Account it is apparent that polyhalovinyl sulfones possess a rich chemistry and are of significant interest as promising synthons. On the other hand, they can be regarded as model compounds for the investigation of subtleties in mechanisms of nucleophilic reactions at the C=C double bond. Both aspects are far from being exhausted and deserve further research leading to better understanding of the fine details of the mechanisms discussed and to uncover further synthetic applications of these compounds.

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