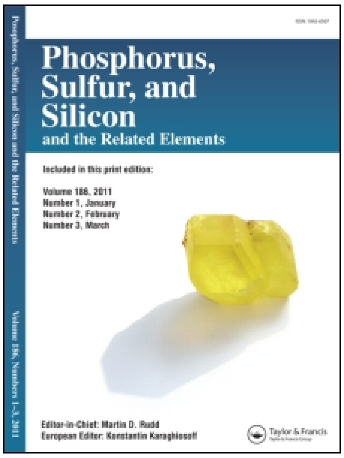

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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To cite this Article Schank, Kurt(1991) 'Sulfones from Mono- and Dithioacetals as Sulfur Chemist'S Tool', Phosphorus, Sulfur, and Silicon and the Related Elements, 58: 1, 207 — 221

To link to this Article: DOI: 10.1080/10426509108040632

URL: http://dx.doi.org/10.1080/10426509108040632

Phosphorus, Sulfur, and Silicon, 1991, Vol. 58, pp. 207–221
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SULFONES FROM MONO- AND DITHIOACETALS AS SULFUR CHEMIST'S TOOL

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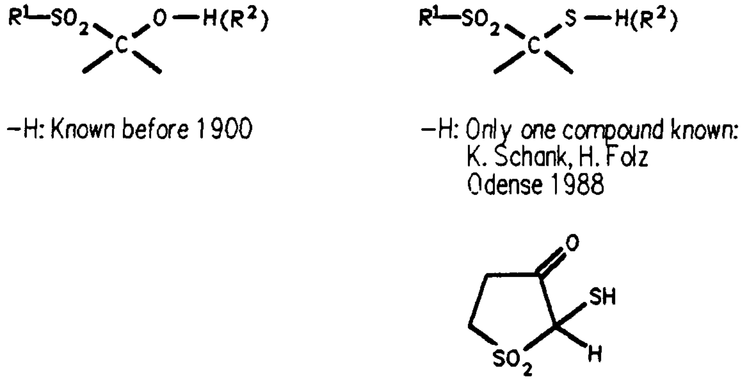
University of Saarland, Saarbrücken, Germany

Abstract Mainly applied syntheses of sulfones of O,S- and of S,S-acetals are briefly summarized; special types of these compounds represent the corresponding ketene acetals. Characteristic reactions all of these classes of compounds - including α sulfonyl carbanions as nucleophiles, α-substituted vinyl sulfones as Michael-acceptors or as cycloaddition partners, especially with regard to their synthon properties - are discussed.

INTRODUCTION

Textbooks on organic chemistry whichever you open, emphasize as main points of view carbon-carbon-connections. Main types of these reactions are interactions of electrophilic with nucleophilic carbon, and the most important species with nucleophilic carbon are carbanions. They are easily prepared from organic halides by the so-called "Umpolung" - i.e. Grignard- or organic lithium compounds - or they are obtained by deprotonation of so-called CH-acidic compounds. A special group of such CH-acidic compounds are sulfones bearing at least one hydrogen α to the sulfonyl group. The resulting α-sulfonyl carbanions are very familiar to sulfur chemists, however, in spite of their importance they are lacking within most text books. They are very conveniently accessible and they are excellent nucleophiles. However, after ensued carbon-carbon-connections, the further presence of the sulfonyl group is undesired in most cases. Thus, the question of an adequate possibility of removal of the auxiliary group arises. Because of the poor nucleofugal tendency[1] of sulfonyl groups, simple eliminations or fragmentations are successful only in exceptional cases. Modern methods[2] of removal of sulfonyl groups utilize reductive eliminations - yielding hydrocarbons -,or oxidative desulfonylations - yielding carbonyl compounds.

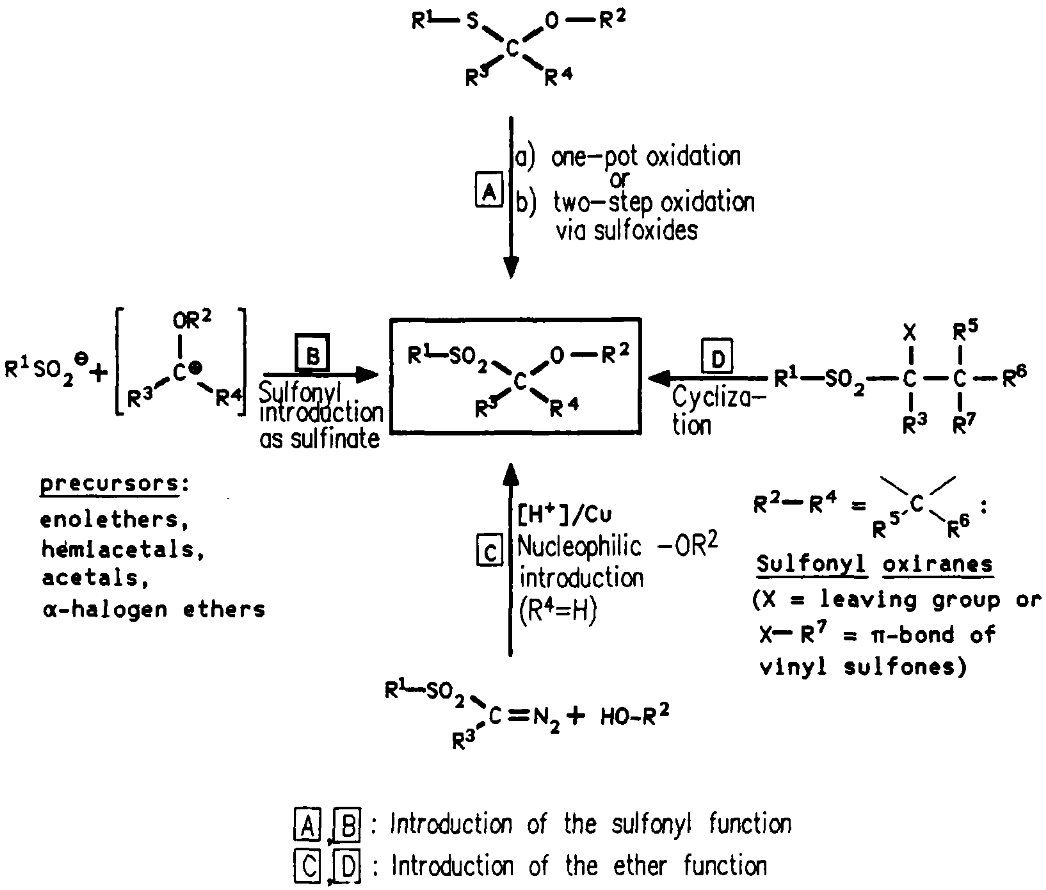
These latter methods occur particularly simple if one starts reactions with CH-acidic sulfones which already contain an additional function in α-position corresponding to a formal oxidation process. Appropriate substances of this kind are the title compounds, they are derivatives of the corresponding α hydroxy- respectively α mercapto-sulfones.



SCHEME 1 Derivates of α hydroxy- and α mercapto-sulfones.

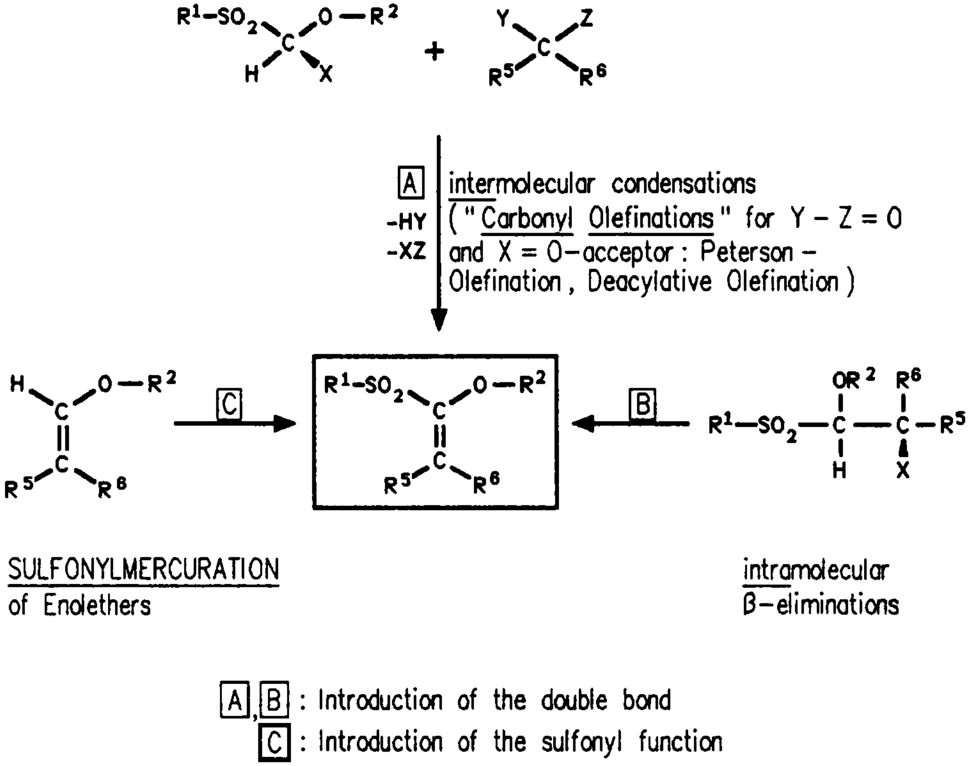
SYNTHESES OF THE TITLE COMPOUNDS

Scheme 2 describes a selection of several synthetic procedures leading to O,S-acetal S,S-dioxides.



SCHEME 2 Generation of α sulfonyl ether (O,S-acetal S,S-dioxides).

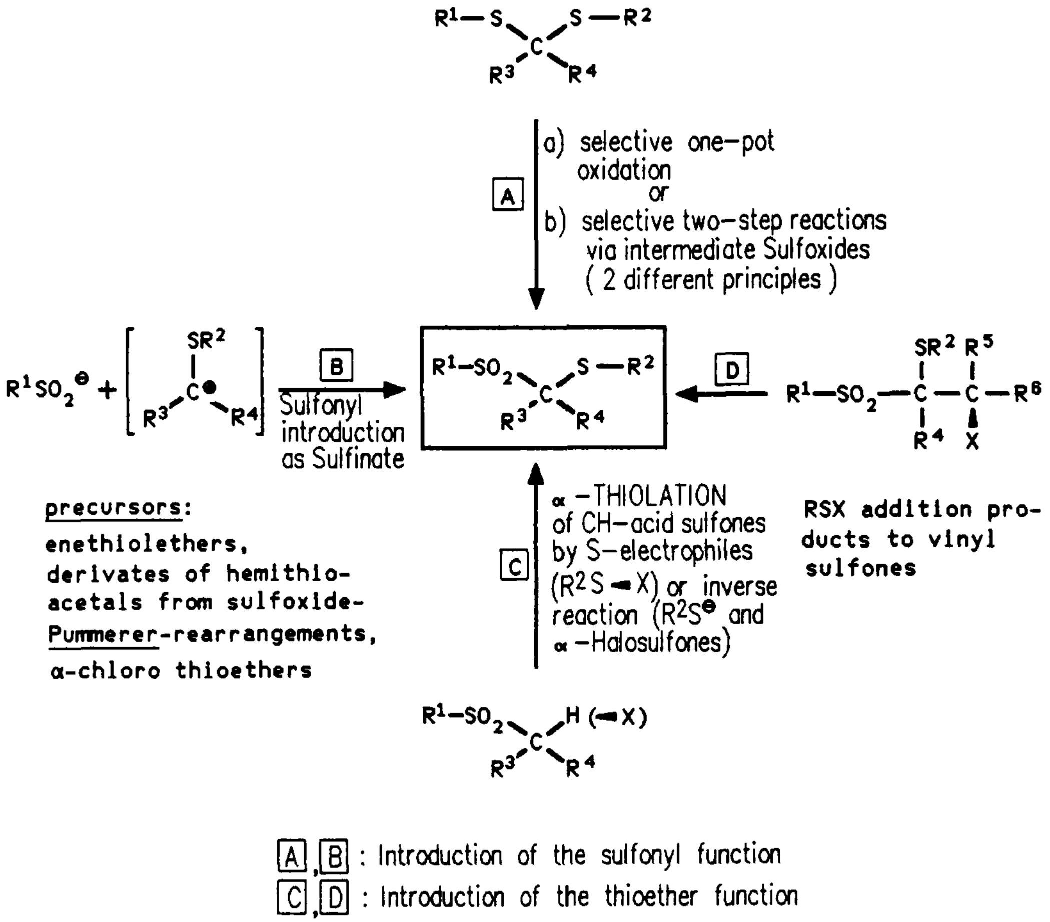
Main pathways are twofold oxidations of O,S-acetals at sulfur (A), introduction of the sulfonyl group by sulfinate S-alkylation with carboxonium precursors (B), or introduction of ether functions into the α-position of appropriate sulfones (C),(D). A particular group of these α sulfonyl ethers are those hypothetically derived from ketene O,S-acetals.



SCHEME 3 Generation of ketene O,S-acetals S,S-dioxides.

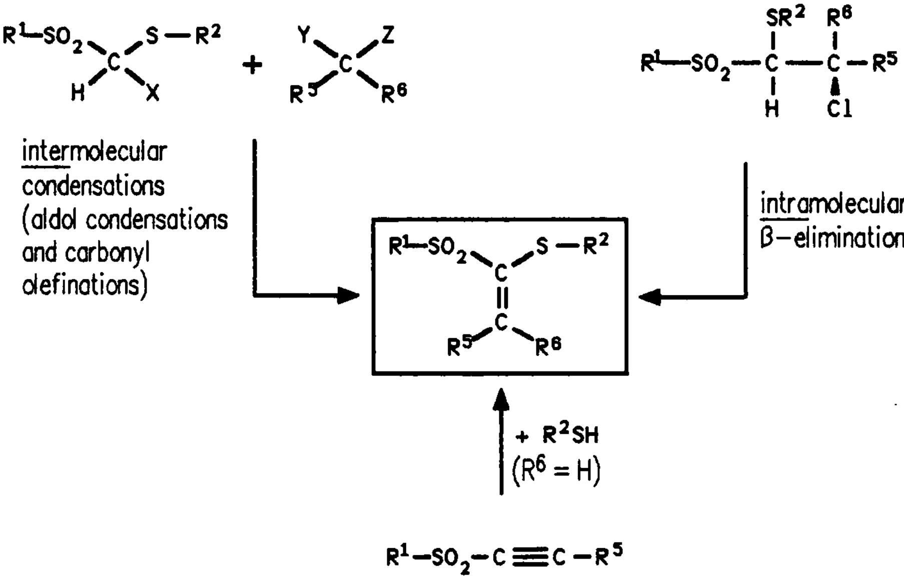
They have been synthesized by us[3] using the method of deacylative olefination. As combinations of vinyl sulfones on the one hand and of enolethers on the other hand, we were interested whether one group would dominate the influence of the other. The result was, the group affects compensate one another.

The second type of our title compounds are the unsymmetrical dithioacetal S,S-dioxides of Scheme 4.



SCHEME 4 Generation of unsym. dithioacetal S,S-dioxides.

Similarly to their O,S-relatives, they can be generated by selective twofold oxidations at one sulfur (A), or by sulfinate S-alkylation with thiocarboxonium precursors (B). A simultaneous formation of a sulfonyl group and a thioether group at the same carbon atom occurs by conversion of appropriate methylene nucleophiles with sulfinyl chlorides[3]. This reaction had been presented by us on the Sulfur Symposium at Nijmegen. Much easier than the corresponding ether function, the thioether function can be introduced α to sulfonyl groups (C),(D). Either electrophilic sulfenylation of α sulfonyl carbanions, or nucleophilic thiolations of adequate sulfones give rise to the target molecules. It cannot be ruled out that both methods lead to a common intermediate step by single-electron-transfer (SET). As in the case of the sulfonyl ethers, we prepared the corresponding ketene dithioacetal S,S-dioxides.

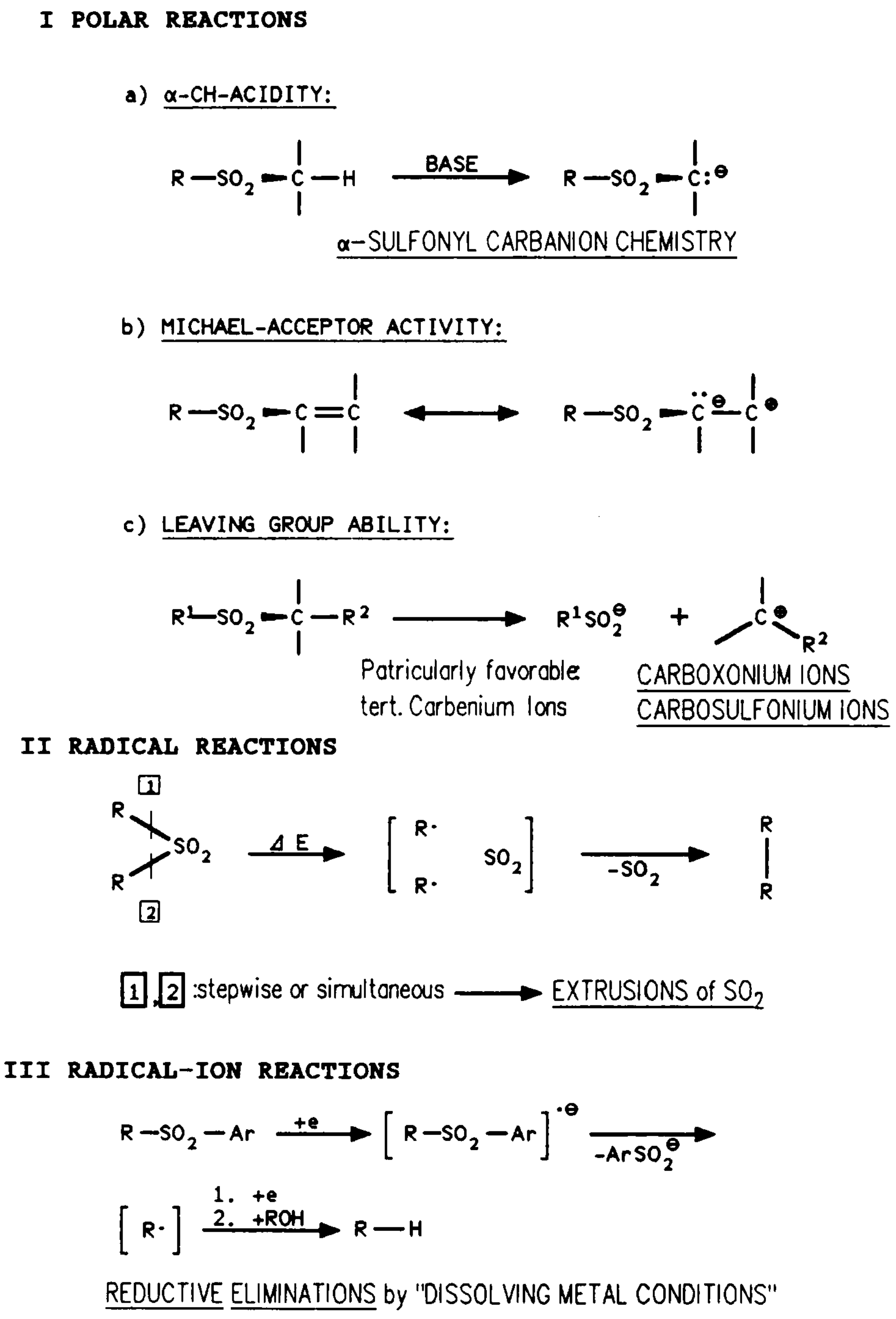


SCHEME 5 Generation of unsym. ketene dithioacetal S,S-dioxides

Differing from the former compounds, the latter behave as very efficient Michael-acceptors[4] as well as cycloaddition reagents.

REACTIONS OF THE TITLE COMPOUNDS

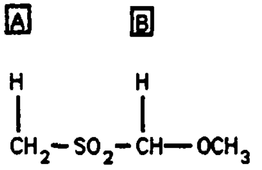
Typical reactions of sulfones include: Polar Reactions, Radical Reactions, and Radical-Ion Reactions.



SCHEME 6 Reactions of sulfones.

For radical cation fragmentations (IV): c.f. MS decay of sulfones[2].

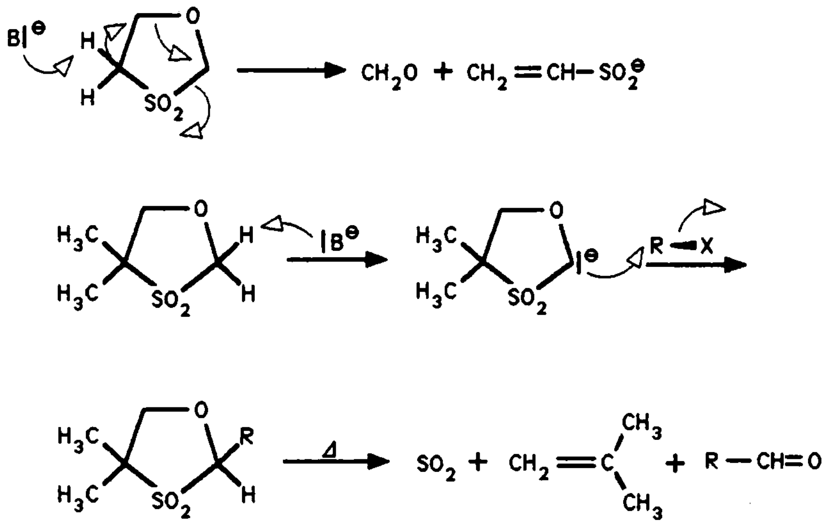
Regardless their substitution by R equal to ether or thioether groups, similar reactions can be observed with the title compounds. Thus, we[5] and others[6] studied the carbanion chemistry of α sulfonyl ethers (alkylations, aldol reactions, acylations, further substitutions with heteroatoms a.s.o.). First of all, we were interested in the relative basicity and nucleophilicity of sulfone α-CH and sulfonyl ether α-CH. Therefore, we prepared methyl methoxymethyl sulfone by different methods and quenched the carbanion mixture - obtained with a molar amount of a strong base - by ethyl benzoate[7]. The result was as follows: With potassium-tert. butylate only a quenching product of (A), with butyl lithium quenching products of anions (A) and (B) as well as a twofold substitution product (A),(B) (ratio of 4:3:4) were obtained.



$$\overset{\boxed{A}}{\overset{H}{CH_2}}-SO_2-\overset{\boxed{B}}{\overset{H}{CH}}-OCH_3$$

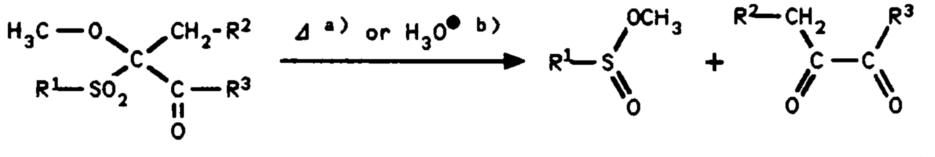
potassium–tert. butylate: anion $\boxed{A}$
butyl lithium: anions $\boxed{A}$ and $\boxed{B}$

To exclude the effect of steric hindrance of the methoxy group on α hydrogens we prepared - as cyclic α sulfonyl ether -unsubstituted 1,3-oxathiolane S,S-dioxide. But its deprotonation resulted in a fragmentation of the cyclic sulfonylether yielding formaldehyde and vinyl sulfinate[8]. This undesired fragmention had been excluded by Gokel and Gerdes[9] by replacement of the troublesome hydrogens toward methyl groups. Thus, the system reached synthon properties by removal of the sulfonyl group as sulfur dioxide[9a]:



SCHEME 7 Fragmentation of cyclic 1,3-oxathiolane S,S-dioxides.

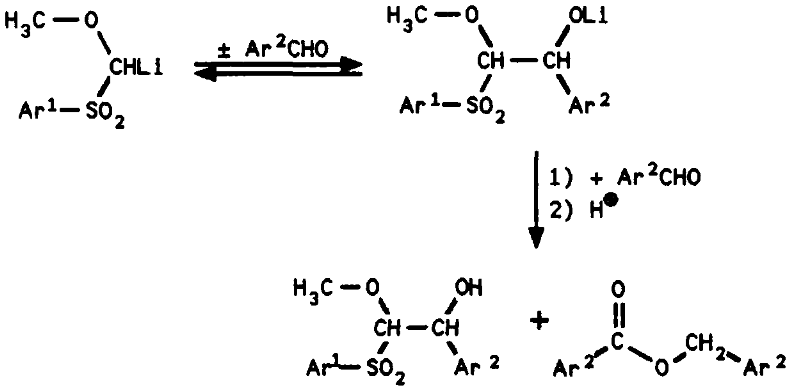
Another possibility to suppress a spontaneous ring fragmentation uses a ring enlargement[9b]. In open chain systems no extrusions of sulfur dioxide have been observed on thermolysis or hydrolysis, instead, together with carbonyl compounds alkyl sulfinate or sulfinic acid are formed[10]:



(i.e. R^1 = 4-Me-C_6H_4, a) 96%) (i.e. R^2 = H; R^3 = Ph, a) ≅ 100%)

SCHEME 8 Thermolysis or hydrolysis of open chain sulfonylethers

The principle of the so-called push-pull-, donor-acceptor-, or - presently in fashion - capto-dative[11] substitution has stimulated organic chemists from the past until today to explain a special stability of certain radicals. Since α sulfonyl ethers bear the features of such a substitution, it was of interest whether their anions could yield suchwise stabilized radicals after an one-electron-oxidation. Anticipated, we could not observe stabilized radicals derived from the title compounds. But in the course of our investigations on aldol additions to anions of α sulfonyl ethers, we observed - depending on the nature of the aldehyde utilized for addition - on the one hand the expected aldol adducts, on the other hand completely unexpected esters as products of an apparent Claisen-Tischtschenko - like aldehyde disproportion reaction[12]; in the course of this latter reaction the starting α sulfonyl ether remained unchanged:

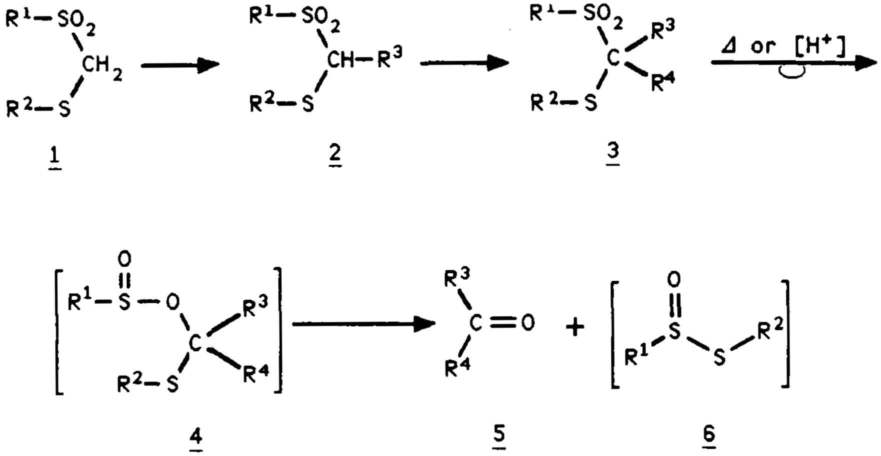


Ar^1 = 4-Cl-C_6H_4;

Ar^2= 4-NO_2-C_6H_4	/	88%
3-NO_2-C_6H_4	21% (m.d.)	39%
4-CF_3-C_6H_4	57% (m.d.)	28%

SCHEME 9 Claisen-Tischtschenko reaction of α sulfonylethers

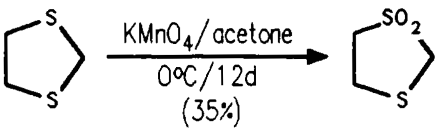
Similar reactions as with O,S acetal S,S-dioxides can be observed with the corresponding monosulfones of dithioacetals. The open-chain representants have been used by us and others[13] in order to synthesize different types of carbonyl compounds on a specific way:



SCHEME 10 O,S-acetal S,S-dioxides as synthons for carbonyl compounds

Syntheses of 2 and 3 need not start from 1, they can ensue also by independent methods. The sulfone-sulfinate-rearrangement from 3 to 4 can be effected by energy transfer and/or acid catalysis[14], the final decomposition of thioalkyl sulfinate 4 resembles the known decomposition pathways of closely related halomethyl or alkoxymethyl carboxylates.

Surprisingly, the basic five-membered monosulfone from 1,3-dithiolane is not described in literature; the hitherto described dioxides don't possess the expected structure. Therefore, we[15] prepared this compound by the method of Gokel[9] and characterized it by usual methods:



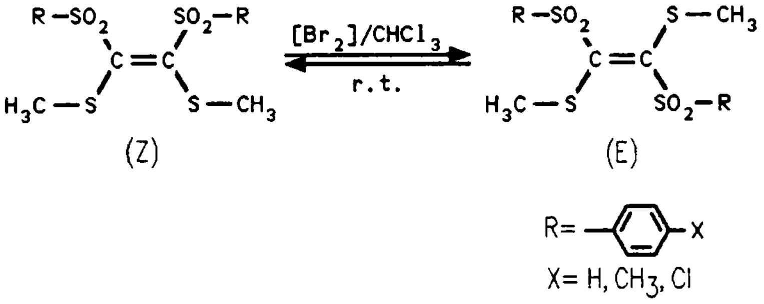
colorless crystalls (ether)
m.p. 73.5°C, δ_{CH_2} 3.865 ppm

SCHEME 11 Preparation of 1,3-dithiolane 1,1-dioxide

Schaumann[16] has applied our cyclofragmentation reaction with substituted 1,3-dithiolane 1,1-dioxides in order to generate different types of thiocarbonyl compounds. Our main interest concerning the title compounds was focussed more on the following 3 aspects:

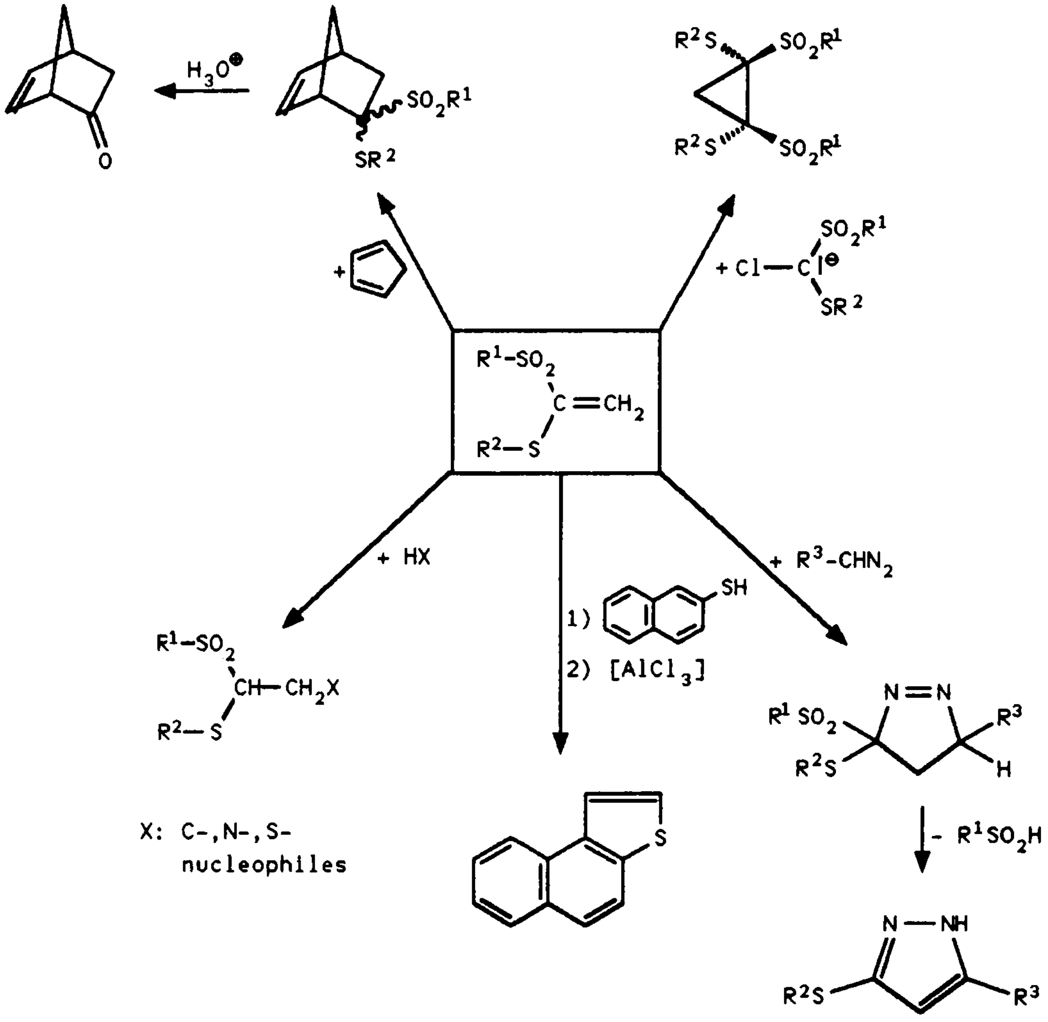
1) The Mechanism of the Sulfone-Sulfinate-Rearrangement
2) Generation and Reactions of Donor-substituted Sulfonyl carbenes
3) Syntheses and Behavior of Ketene O,S- and S,S-acetal S,S-dioxides

The main results to point 1) have been already discussed, results to point 2) have been presented on the Riga Sulfur Symposium and have been published in part recently[17], as last result we were successful in synthesis of the apparent dithio carbene dimers which show facile Z,E-isomerizations[15]:



SCHEME 12 Z,E-Isomerization of the dithio carbene dimer

As to point 3), ketene O,S-acetal S,S-dioxides have been equally mentioned before, the unsubstituted methylene compound is rather inreactive and served us only for a synthesis of sulfonyl formates by ozonolytic cleavage[18]. The corresponding dithio analogs proved to be completely different in reactivity. On the one hand they are excellent Michael acceptors which show generally additions of HX-compounds whose anions are sufficiently nucleophilic, to the double bond, on the other hand they are interesting cycloaddition partners[19]:



SCHEME 13 Reactions of ketene O,S-acetal S,S-dioxides

Finally, to evaluate the discussed classes of compounds, one can state: α sulfonyl ethers are conveniently prepared, their anions, however, show a more basic than nucleophilic character; the corresponding ketene derivatives are rather unreactive. From a preparative point of view, dithioacetal S,S-dioxides are more interesting because of their higher carbanion nucleophilicity; their syntheses need a good hood because of the unpleasant thiol odor; the chemistry of the corresponding ketene derivatives, however, is suchwise interesting that one can risk also unpleasant odors, and further investigations on these compounds are in progress presently in our laboratory.

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