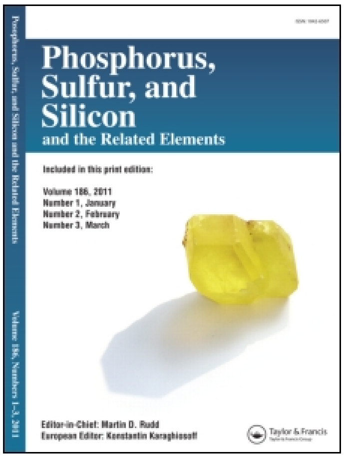

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# New Sulfurchemistry Symposium Abstracts

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# NEW SULFUR CHEMISTRY SYMPOSIUM. ABSTRACTS

## DIRECT SUBSTITUTION *VS.* ELIMINATION–ADDITION MECHANISMS IN SUBSTITUTION REACTIONS OF ALKYL α-DISULFONES AND SULFINYL SULFONES.

JOHN L. KICE, OSCAR FARNG and SHI-MING WU. *Department of Chemistry, Texas Tech. University, Lubbock, Texas 79409.*

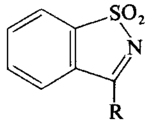
In principle nucleophilic substitution reactions of alkyl α-disulfones ($RSO_2SO_2R$) may take place either by direct substitution (Eq. 1a) or by an elimination–addition mechanism with a sulfene as an intermediate (Eq. 1b). Examination of reactions of a series (R = Me, *n*-Bu, *i*-Pr) of alkyl α-disulfones shows that with most nucleophiles substitution occurs by the elimination–addition mechanism. However, when the nucleophile is one, like azide ion, which is weakly basic but strongly nucleophilic, the direct substitution pathway is used. In the case of substitution reactions of alkyl sulfinyl sulfones, $RS(O)SO_2R$, leading to sulfinyl derivatives, RS(O)Nu, the direct substitution pathway is used exclusively, even with those nucleophiles most prone to react via the elimination–addition pathway with the α-disulfones. Rate data for many of the above reactions will also be discussed.

$$\begin{tikzcd}
 & R'CH_2SO_2^- + R'CH_2SO_2Nu & & \text{(1a)} \\
R'CH_2SO_2SO_2CH_2R' + Nu^- \arrow[ur] \arrow[dr] & & & \\
 & R'CH_2SO_2^- + NuH + R'CH{=}SO_2 \arrow[r, "NuH"] & R'CH_2SO_2Nu & \text{(1b)}
\end{tikzcd}$$

## SYNTHETIC APPLICATIONS OF THE 1,2-BENZOISOTHIAZOLE 1,1-DIOXIDE RING SYSTEM.

R. A. ABRAMOVITCH, P. C. SRINIVASAN, K. MORE, and J. STOWERS, *Department of Chemistry and Geology, Clemson University, Clemson, SC 29631 and University of Alabama, University, Alabama 35486.*

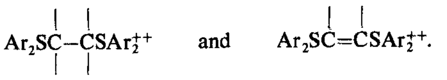
The 1,2-benzoisothiazole 1,1-dioxide ring system (**1**) (where R = alkyl, aryl, Cl, OR, SR) is now readily available. It undergoes a variety of interesting reactions which lead to six-, seven-, or polycylcic ring systems and these will be described. In particular, the ring expansions to (2*H*)-1,2-benzothiazine-4(3*H*)-one 1,1-dioxides and to 1,2-benzothiazepine 1,1-dioxides will be discussed. The latter compounds are remarkably stable to a variety of oxidative, reductive, basic and alkylative conditions and the possibility that the seven-membered sultam ring represents a new type of aromatic system is considered. Evidence relating to this will be presented. When R is a vinyl group the resulting conjugated system undergoes [4 + 2] cycloadditions to give fused *N*-sulfonyl-1,4-dihydropyridines, which then rearrange spontaneously to the corresponding 1,2-dihydropyridines.



(**1**)

## ORGANOSULFUR CATION RADICAL CHEMISTRY. HENRY J. SHINE, *Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.*

Two aspects of the chemistry of organosulfur cation radicals (designated as $Ar_2S^{\cdot+}$) will be presented. In the first, the reaction of thianthrene and phenoxathiin cation radicals with organometallics ($R_2M$) and with alkenes and alkynes will be described. These reactions, discovered only in recent years, lead respectively to sulfonium ions $(Ar_2SR)^+$ and to adducts of the type:

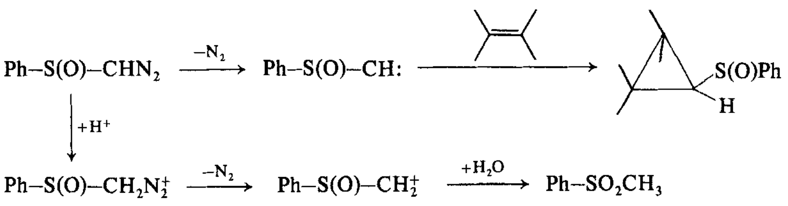


$$\mathrm{Ar_2SC{-}CSAr_2^{++}} \quad \text{and} \quad \mathrm{Ar_2SC{=}CSAr_2^{++}}.$$

The second aspect will be the reconsideration and explanation of a long-known puzzle in organosulfur chemistry: the way in which aromatic and heterocyclic sulfoxides (designated as $Ar_2S{=}O$) are converted into the deoxy-cation radicals ($Ar_2S^{\cdot+}$) in acid solution. It will be proposed that this conversion is quite complex and involves a series of redox reactions between $Ar_2S^{++}$ and hydroxylated $Ar_2S$. Spectroscopic and product evidence will be presented.

## α-DIAZO SULFOXIDES. CLIFFORD G. VENIER, MARK A. WARD, HOWARD J. BARAGER and FEAGIN A. WING. *Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129.*

*α*-Diazo sulfoxides are useful both synthetically and as precursors to sulfinyl carbenes and what are likely sulfinyl carbonium ions.



Phenyl sulfinyl carbene is conveniently generated by thermal decomposition of phenyl diazomethyl sulfoxide at room temperature. Rate studies establish that the intermediate in sulfinyl cyclopropanations is the carbene and that it is surprisingly selective. This selectivity arises from the fact that the sulfinyl function can stabilize the carbene both by inductive electron withdrawal and by a hitherto little noted powerful resonance donation.

Phenylsulfinyl carbonium ion, implicated in the acid-catalyzed decomposition of the diazo compound, has also been generated by silver-assisted solvolysis of phenyl iodomethyl sulfoxide. In both cases, the eventual product is phenyl methyl sulfone, which likely arises by nucleophilic attack on the electrophilically ambident cation at sulfur.