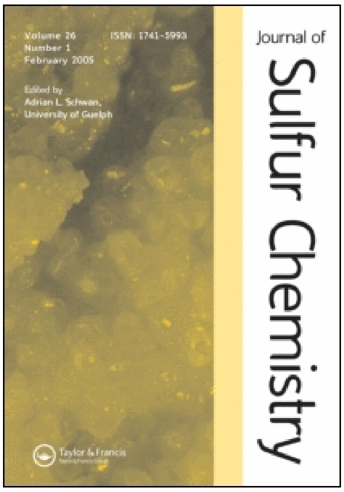

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Forty Years in Organosulfur Chemistry

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FORTY YEARS IN ORGANOSULFUR CHEMISTRY

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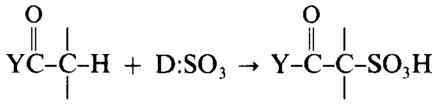
Sulfur Reports is pleased to add another distinguished chemist to those who have contributed autobiographical accounts of their significant contributions to organic sulfur chemistry. William E. Truce, now Professor Emeritus of Chemistry at Purdue University, was born in 1917 in Chicago, Illinois. He received the B.S. degree at the University of Illinois and the Ph.D. with the celebrated organic sulfur chemist C. M. Suter at Northwestern University. After one year of teaching at Wabash College and two as a research chemist at Swift and Co. he joined the faculty of Purdue. Along with his rise through the ranks to Professor of Chemistry in 1956, he was Assistant Dean of the Graduate School, the Executive Officer for the 1961 National Organic Symposium, Chairman of the 1964 Gordon Research Conference on Organic Reactions and Processes, President of the Purdue Chapter of Sigma Xi, Secretary, Purdue Chapter of Phi Beta Kappa, recipient of several teaching awards, and a Guggenheim Fellow at Oxford in 1957. Professor Truce outlines contributions he and his students have made to the classes of sulfones, sulfenes, sulfinic acids, sulfonyl iodides, α-alkylsulfonyl compounds, sultones, vinyl and acetylenic halides, *S*-ylides, and S-stabilized carbanions. Among reactions illustrated are sulfonation, reduction with Li-$MeNH_2$, radical anion reactions, cycloadditions, nucleophilic additions and displacements, and rearrangements including, of course, the Truce-Smiles rearrangement. Many of the topics have significant synthetic applications, and several have important stereochemical features.

Over these past forty plus years, the great variety of organic sulfur compounds and the diversity of phenomena exhibited by them have provided a fertile training ground for my students to learn the techniques of organic chemistry and the joys/successes as well as the pitfalls/disappointments associated with research.

One of our earliest projects involved studying direct sulfonation as a potential synthetic method for α-sulfo carbonyl systems.[1]



$$\mathrm{Y\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{|}{C}}-H + D{:}SO_3 \rightarrow Y-\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{|}{C}}-SO_3H}$$

$$Y = R, H, HO;\ D = \text{dioxane}$$

It was found that the dioxane-sulfur trioxide reagent was effective for converting various ketones, aldehydes and carboxylic acids to their α-sulfo derivatives.

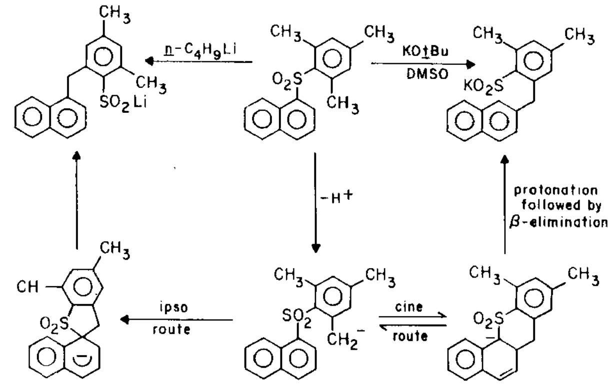
Another early project followed up Purdue's tradition in halogenation chemistry by studying the direct chlorination of sulfides as an approach to α-halogenated sulfides using $SOCl_2$ and SO_2Cl_2 for better control than is had with Cl_2.[2] For example, methods were developed for all nine of the possible chlorinated dimethyl sulfides, and for oxidation to their respective sulfones. Also, several of the chlorinated sulfides were converted to their fluorinated derivatives, a particularly favorable case being

$$Cl_2CHSCCl_3 + SbF_3 \rightarrow F_2CHSCF_3\ (\sim 50\%)$$

Incidentally, this pentafluorodimethyl sulfide, in contrast to some of the less fluorinated sulfides, resisted oxidation to its sulfone.

It was at about this point that we began our studies on metalations of arenesulfonyl systems[3] and the behavior and synthetic utility of such sulfur-stabilized carbanionide structures. After noting that treatment of diphenyl sulfone with butyllithium resulted in metalation at an *ortho* position, we examined the effect of substituent groups on the point of metalation. With bromine substituents, such as the bromodiphenyl sulfones, competitive halogen-metal exchange reactions caused us to abandon heteroatom substituents and restrict further metalation studies to methyl-substituted arenesulfonyl systems.

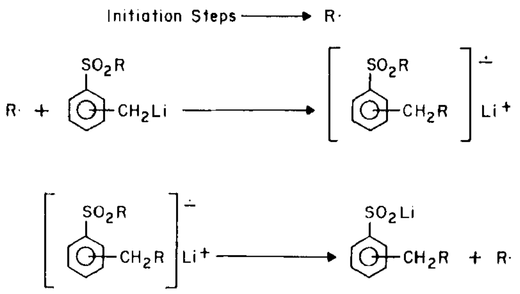
Particularly interesting was a methyl substituent in the ortho position, as with *o*-tolyl phenyl sulfone, for now metalation took place at the ortho benzylic position, rather than an open ortho position. Of even greater interest was the fact that warming of that metalated species resulted in a novel rearrangement reaction, which was dubbed by others as the Truce-Smiles rearrangement. One of the interesting examples of this rearrangement is that of α-naphthyl mesityl sulfone. Treatment of the sulfone with *n*-butyllithium in ether or with potassium *t*-butoxide in DMSO results in *o*-benzylic metalation followed by migration of the naphthyl group to that benzylic position either with retained α-naphthyl orientation (*ipso* route) or changed orientation to β-naphthyl (*cine* route), respectively, as outlined in Scheme I; both routes are considered to be Truce-Smiles rearrangements.



SCHEME I

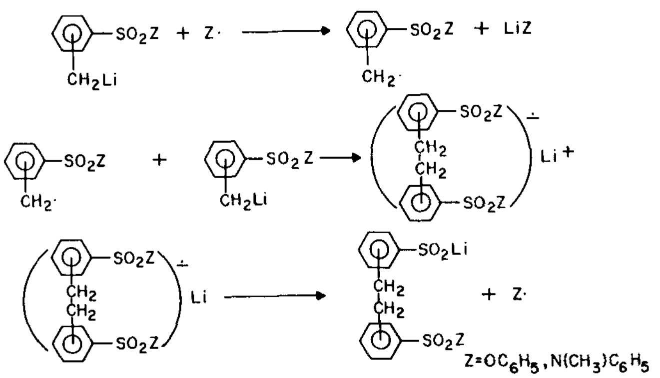
Several years ago, such rearrangement was extended to *o*-tolyl *t*-butyl sulfone, which undergoes benzylic metalation followed by migration of the *t*-butyl group to give, after acidification, *o*-neopentylbenzenesulfinic acid. An even more facile rearrangement occurs with the para isomer as generalized in Scheme II, shown with the tentative radical radical anion chain mechanism.[4]

Another remarkable reaction displayed by benzylically metalated arenesulfonyl systems is a coupling condensation process on phenyl arenesulfonates and arenesulfonanilides. The reaction, which we published for ortho systems in 1978, was extended to para isomers, as summarized in Scheme III. The proposed mechanism for these coupling condensations is similar to that for the alkyl migrations of Scheme II except for the added electron transfer step.[5]



SCHEME II

These rearrangements of diaryl sulfones and alkyl aryl sulfones and coupling condensations of phenyl arenesulfonates and arenesulfonanilides offer synthetic potential for forming carbon-carbon bonds between benzylic carbon and aryl, alkyl or benzylic units, respectively.



SCHEME III

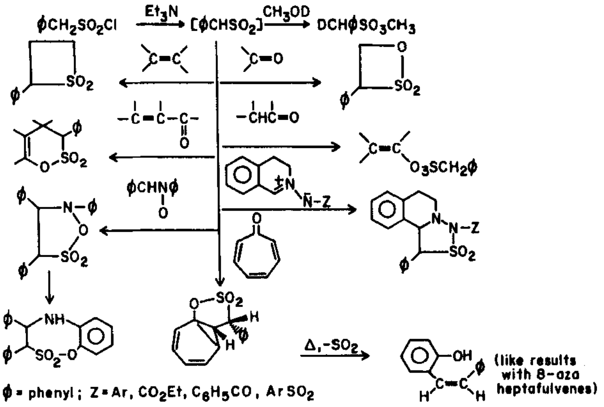
Still another area of organosulfur chemistry, which occupied much of our attention, involved reactions of sulfenes (reactive intermediates generated most conveniently by treatment of sulfonyl chlorides with triethylamine) with unsaturated polar substrates.[6] Via such cycloadditions and depending upon the nature of the polar substrates, one can generate cyclic sulfones, sultones and sultams in a variety of ring sizes (four, five, six and even seven) as suggested in Scheme IV.

Even earlier studies on reactions of thiols under basic conditions with acetylenic and vinylic halide-type substrates led to such observations as:

1. *trans*-Stereoselectivity of thiolate (and amine) additions to activated acetylenes,[7] as in

$$p\text{-}O_2NC_6H_4C{\equiv}CH + p\text{-}CH_3C_6H_4SNa \xrightarrow{CH_3OH} (Z)\text{-}p\text{-}O_2NC_6H_4CH{=}CHSC_6H_4CH_3\text{-}p$$

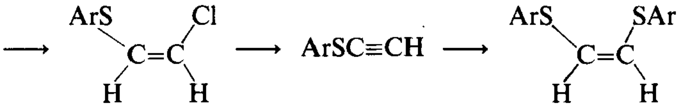
100% stereoselective



SCHEME IV

2. Among the several mechanisms by which nucleophilic displacements on vinylic halides occur is an elimination-addition sequence where the anti character of the E_2 process as well as the anti character of the nucleophilic addition process form the basis of the following result:[8]

$$\text{N.R.} \xleftarrow{(E)\text{-CHCl=CHCl}} \text{ArSNa, EtONa, EtOH} \xrightarrow{(Z)\text{-CHCl=CHCl}} \text{HC}\equiv\text{CCl}$$



3. In the course of certain of these nucleophilic addition processes, a new method of preparing sulfinic acids[9] from the readily available thiols was developed as summarized in the reaction sequence,

$$\text{RSH} + \text{CH}_2\text{=CHCN} \xrightarrow{\text{base}} \text{RSCH}_2\text{CH}_2\text{CN} \xrightarrow[\text{CH}_3\text{CO}_2\text{H}]{\text{H}_2\text{O}_2} \text{RSO}_2\text{CH}_2\text{CH}_2\text{CN}$$

$$\xrightarrow[-\text{RSCH}_2\text{CH}_2\text{CN}]{\text{RSNa, EtOH}} \text{RSO}_2\text{Na}$$

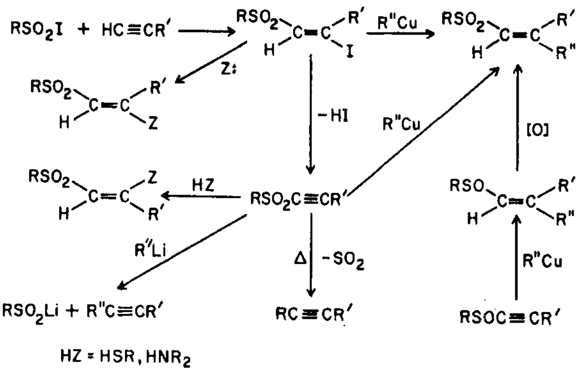
4. After noting the trans stereoselectivity[10] of additions of sulfonyl iodides to acetylenes, we examined the potential[11,12] of those adducts and their derivatives as possible synthons as partly outlined in Scheme V.

With the hope of further enhancing the synthetic utility of the aforementioned sequences, we briefly pursued reductive cleavages of sulfides and sulfones by dissolving metals,[13] i.e.,

$$\text{ArSO}_n\text{R} + \text{e's (from dissolving metal)} \longrightarrow$$

$$(\text{ArSO}_n\text{R})^- / (\text{ArSO}_n\text{R})^= \longrightarrow \text{cleavage products}$$

Among the systems studied was a series of sulfones, $C_6H_5SO_2R$, cleaved by lithium in methylamine. Cleavage occurred predominantly at the alkyl-sulfur bond with tertiary alkyl groups, but predominantly at the aryl-sulfur bond with primary alkyl groups.[14]



SCHEME V

Also of potential synthetic value for the α-alkylation of sulfonyl structures,[15] and based on some of Professor H. C. Brown's work with organoboranes, is the following conversion:

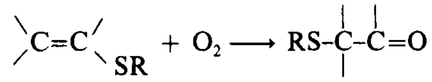
$$R_3B + BrCH_2SO_2Y \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} RCH_2SO_2Y$$

$$Y = C_6H_5,\ C_2H_5,\ OCH_2C(CH_3)_3,\ N(C_2H_5)_2$$

Additional synthetic methods involved sulfur ylides and sulfur-stabilized carbanions for preparing (1) cyclopropanes,[16,17,18] (2) stabilized sulfur ylides,[19] (3) α-nitrosulfonyl systems and their α-bromo derivatives,[20] (4) α-alkylated sulfonyl systems,[21] (5) diastereomeric β-hydroxy sulfones,[22] (6) α-acylated sulfur systems,[23,24,25,26] (7) α,β-epoxysulfonamides,[27] and (8) α-sulfonyl sulfonic esters.[28]

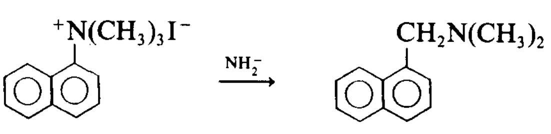
Several studies on sultones established rearrangement during their formation from hydroxysulfonic acids, and their utility in preparing ω-sulfo systems by Friedel-Crafts operations and through other ring-opening nucleophilic displacements on the sultone grouping.[29,30] Still other Friedel-Crafts studies involved (1) the preparation of α-tetralone directly by using butyrolactone,[31] (2) the use of vinylic sulfones as alkylating agents,[32] and (3) the preferred formation of a five-membered (rather than six-membered) cyclic sulfone with an appropriate alkanesulfonyl chloride.[33]

Additional interesting rearrangements were encountered as summarized by the following equations:

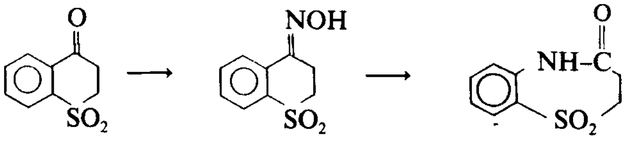


$$>C=C<_{SR} + O_2 \longrightarrow RS\text{-}C\text{-}C{=}O$$

(Ref. 34)

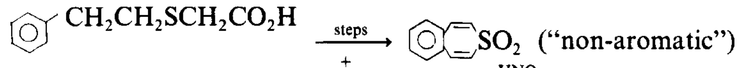


(Ref. 35)



(Ref. 36)

Lastly, several other investigations are outlined below, in equation form.



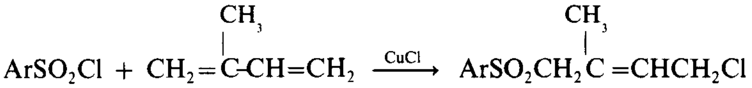
(Ref. 37)

$$C_6H_5CH{=}CH\overset{+}{N}(CH_3)_3X^- \xrightarrow{HNO_3}$$

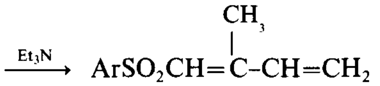
$$o/p\text{-}O_2NC_6H_4CH{=}CH\overset{+}{N}(CH_3)_3X^-$$ (Ref. 38)

$$RSO_2CH{=}CH_2 + ArN_2Cl \longrightarrow RSO_2CHClCH_2Ar$$

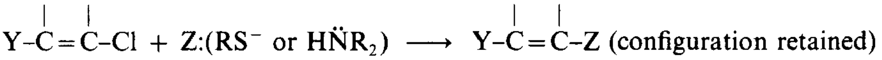
$$\xrightarrow{\text{base}} RSO_2CH{=}CHAr$$ (Ref. 39)



$$ArSO_2Cl + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{-}CH{=}CH_2 \xrightarrow{CuCl} ArSO_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCH_2Cl$$



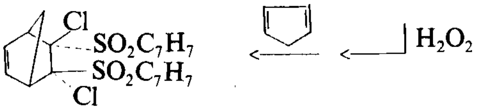
$$\xrightarrow{Et_3N} ArSO_2CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{-}CH{=}CH_2$$ (Ref. 40)



$$Y\text{-}\overset{|}{C}{=}\overset{|}{C}\text{-}Cl + Z{:}(RS^- \text{ or } H\ddot{N}R_2) \longrightarrow Y\text{-}\overset{|}{C}{=}\overset{|}{C}\text{-}Z \text{ (configuration retained)}$$

$$(Y = CO_2Et, SO_2Ar, CN, PhCO)$$ (Ref. 41)

$$C_7H_7SNa + Cl_2C{=}CCl_2 \xrightarrow{EtOH} trans\text{-}C_7H_7SCCl{=}CClSC_7H_7$$ (Ref. 42)



In conclusion, I should like to express my deep appreciation to

1. my many students, to whom I am indebted for any successes achieved, for they carried out the time-consuming experimental work;

2. the fine faculties at the University of Illinis, notably Professor Carl S. Marvel (now deceased), who taught me my first course in organic chemistry, and at Northwestern University, notably Professor C. M. Suter (now deceased), who introduced me to the organic chemistry of sulfur, and Professor C. D. Hurd, for his friendly encouragement;

3. the service/support staff at Purdue University – "I couldn't have done it without you";

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The above is but a sampling of the references pertaining to the respective topics; additional references are cited therein.