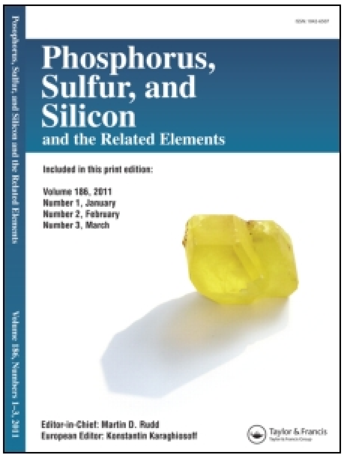

Phosphorus, Sulfur, and Silicon and the Related Elements
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Leterature Highlights

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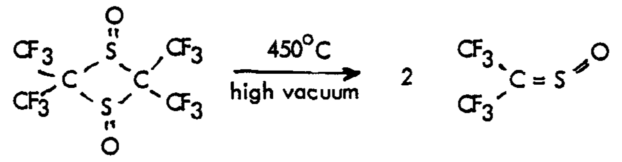
LITERATURE HIGHLIGHTS

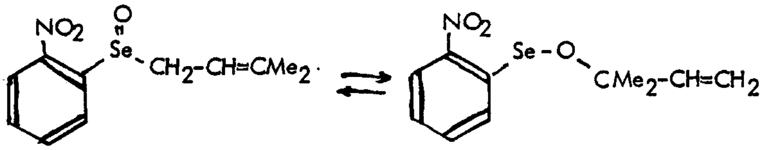
Contributions may be forwarded in duplicate to any one of the editors. Drawings and structures must be neatly and compactly prepared in ink for *direct* photoreproduction. All abstracts must be in English with double-spaced, typed text, including complete reference source of the abstract at the end. Preparers are not acknowledged.

Simple sulfur compounds can continue to excite interest, especially unsaturated systems that can be useful building blocks increasing the scope of organic synthesis. **The first perfluoroalkyl sulfine**, $(CF_3)_2C{=}S{=}O$, b.p. 58°C, adds to the simpler analogues CH_2SO and CF_2SO, and more complex structures all depending on stabilization of the sulfine grouping by aromatic or heteroaromatic groupings or by an adjacent hetero-atom (S, P, or N). High-vacuum pyrolysis provides simple access:



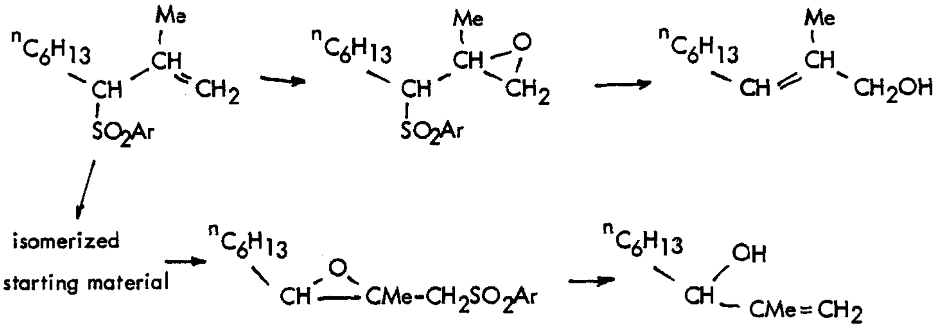
(A. Elsässer and W. Sundermeyer, Tet. Lett., ***24****, 2141, 1983).*

Some of the more dramatic differences between sulfur and selenium are shown in comparisons of sulfoxides with those of selenoxides. A **kinetic study of the selenoxide–selenenate rearrangement**, with the sulfur system in parallel, has been reported by Reich and co-workers and detailed thermodynamic parameters have been evaluated. Going beyond the synthetic applications into the physico-chemical area has considerable benefits to confer, in this case the prediction of efficient asymmetry



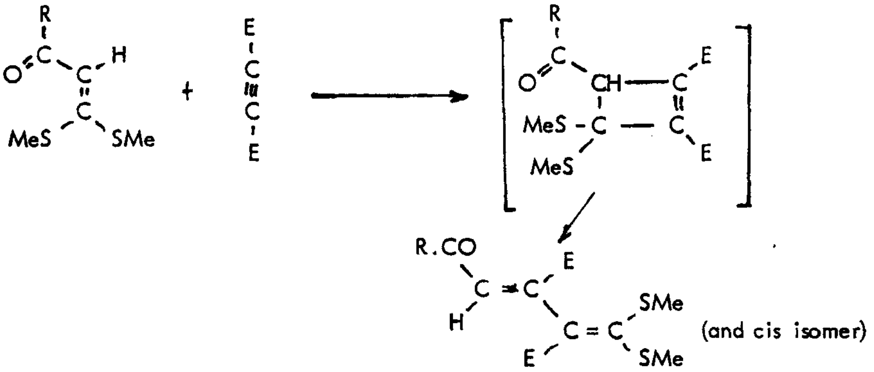
transfer from chiral sulfur to chiral carbon (if there is one) of the sulfenate. This efficiency has not yet been realized, but the prediction will encourage further attempts. *(H. J. Reich, K. E. Yelm and S. Wollowitz, J. Am. Chem. Soc., **105**, 2503, 1983).*

The sulfone group exerts contrasting **influences on reactions** of an allylic carbon–carbon double bond, seen in the competition between 1,3-allylic rearrangement and double bond isomerization which accompanies epoxidation. The reagent for this reaction is *m*-chloroperbenzoic acid in aqueous $NaHCO_3$, and the lack of stereochemical integrity is accounted for by radical steps:



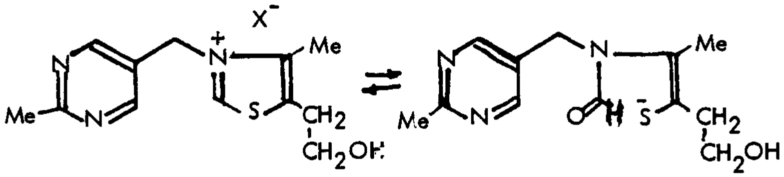
(P. Kocienski, J. Chem. Soc., Perkin Trans. I, 945, 1983).

A polarized **ketoketene dithioacetal** is an effective partner in cycloaddition reactions:



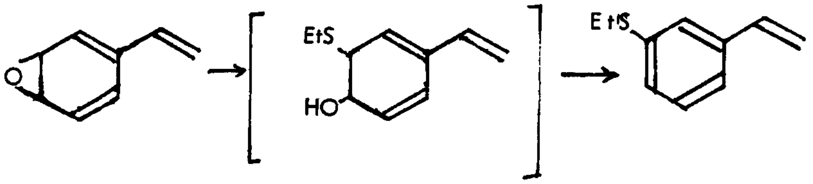
(J. N. Vishwakama, H. Ila and H. Junjappa, J. Chem. Soc., Perkin Trans. I, 1099, 1983).

Ring-opening of the thiazolium ring of thiamine has long been a topic for study, but only through the pH-jump technique in chemical relaxation can the **N-formyl thioenolate** be seen now to exist in significant amounts in aqueous solutions. At pH 9.2–9.4, this ring-opened form is present to the extent of 16% of the overall thiamine content of an aqueous solution, but in considerably smaller amount in neutral solutions.



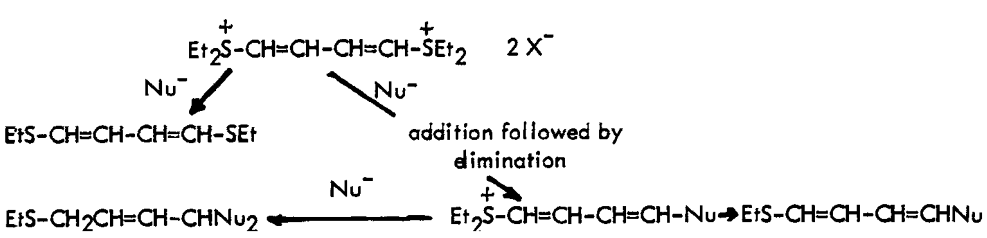
*(J.-M. El Hage Chahine and J.-E. Dubois, J. Am. Chem. Soc., **105**, 2335, 1983).*

The potent mutagen and cytotoxin, styrene-3,4-oxide, reacts with a nucleophile at all ring sites open to it. The major product with ethanethiol is **ethyl *m*-vinylphenyl sulfide** and the para isomer is formed in similar amount, whereas the orthoisomer is a minor product. The results prove that the initial nucleophilic adducts dehydrate to the products without the intervention of S-ethylthiiranium ion intermediates.



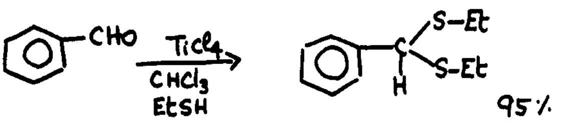
(T. Watabe, A. Hiratsuka, T. Sone and T. Ishihama, J. Chem. Soc., Chem. Commun., 585, 1983).

The sulfonium group, described by Stirling as "the most versatile function in organic chemistry," is seen in action in a substantial study of **buta-1,3-diene-1,4-bis-sulfonium salts** in reactions with common nucleophiles. 1,4-Addition followed by elimination of sulfonium groups, in competition with degradation of the sulfonium groups to the corresponding sulfides, account for all products, but patterns of reactivity depend strongly on the nucleophile.



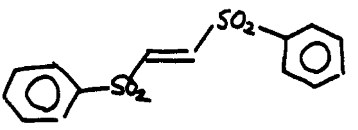
(P. J. Duggan, J. L. Leng, D. R. Marshall and C. J. M. Stirling, J. Chem. Soc., Perkin Trans. I, 933, 1983).

Titanium tetrachloride is now reported to be a clean and efficient catalyst for the preparation of **dithioacetals from aldehydes and ketones**. Reactions are carried out in chloroform solutions and at ambient temperatures. Near quantitative yields of products are obtained from fast and clean reactions. For example benzaldehyde gives a 95% yield of the diethyldithioacetal in an hour.



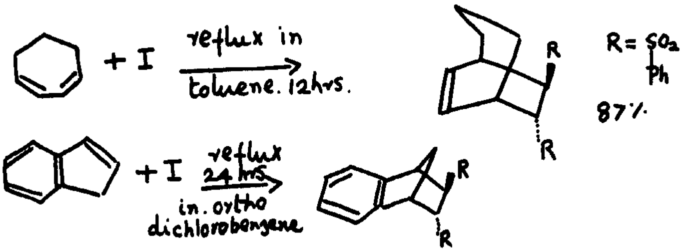
Ketones appear to react slower. Cyclohexanone forms the diethyldithioacetal in 98% yield but the reaction requires 6 hours for completion. The mildness of conditions and the high yields of products are appealing features of this new method of ketalization. It may receive wider application in synthesis involving acid-sensitive carbonyl compounds *(V. Kumar and S. Dev, Tet. Lett., **24**, 1289–92, 1983).*

***Trans*-1,2-bis(phenylsulfonyl)ethylene** (I) is shown to be a viable alternative to maleic anhydride in **Diels-Alder reactions.**



I

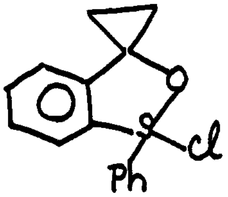
The bis-sulfone is thermally stable and reacts with even the "typical unreactive dienes." The following two examples are illustrative of its application:

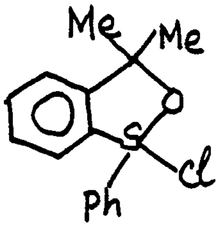


The sulfone groups are readily removed subsequently by reduction with 2% sodium amalgam in methanol buffered with NaH_2PO_4. The synthetic utility of I may be quite extensive *(O. De Lucchi and G. Modena, Tet. Lett., **24**, 1653–56, 1983).*

An impressive example of **steric effects in the hydrolysis of sulfuranes** I and II is described.

I

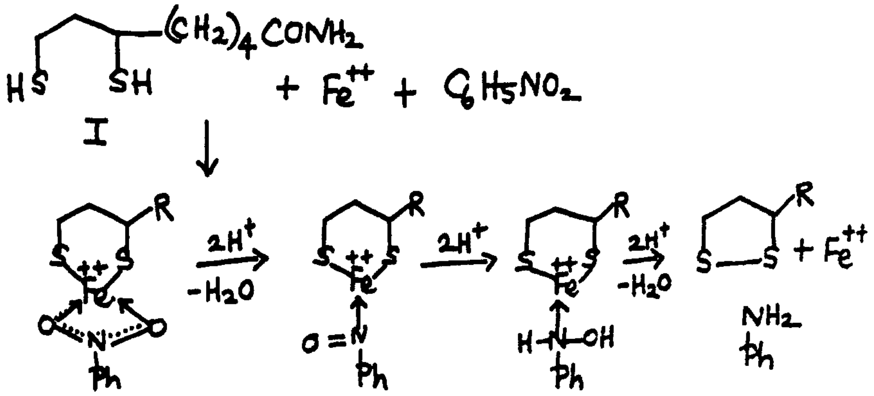




II

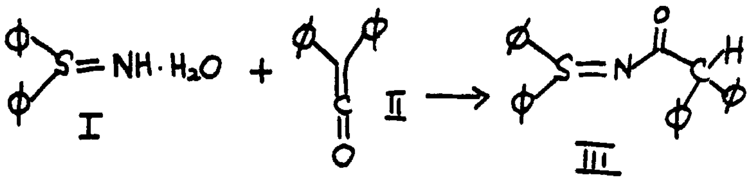
The change in the rates of hydrolysis was followed by ^{13}C NMR. In deuteriochloroform solution, an equimolar mixture of I and II was treated with one equivalent of D_2O. The sulfurane I had a half-life of 14 min, whereas sulfurane II was only 52% hydrolyzed even after nearly 16 days. This rate enhancement shown by I over II "is an intriguing result, regardless of the explanation" based on steric or electronic grounds. The electron-withdrawing character of the cyclopropyl group should make I less reactive than II but the facts are to the contrary. The authors offer an alternative rationale based on steric factors. *(Arun K. Data and Peter D. Livant, J. Org. Chem., 48, 2445, 1983).*

Dihydrolipoamide (I) is shown to be a clean **selective reducing agent for nitrobenzenes, nitrosobenzenes and phenylhydroxylamines**. In the presence of ferrous ion as a catalyst, anilines were formed in good yields and under mild conditions. The authors postulate that the reaction proceeds through the following sequence of reactions.

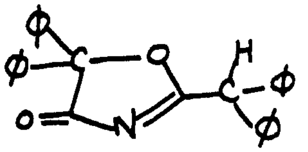


The DHLAm—Fe^{++} reduction is selective and does not affect other functional groups like aldehydes, ketones or olefins. *(Masashi Kijima, Yoko Nambu, Takeshi Endo and Makoto Okawara, J. Org. Chem., 48, 2407, 1983).*

A novel **synthesis of oxazolinones** utilizes the condensation between S,S-diphenylsulfilimine (I) and diphenylketene (II). When equimolar amounts of I and II react at 0°, the product is the sulfilimine (III):



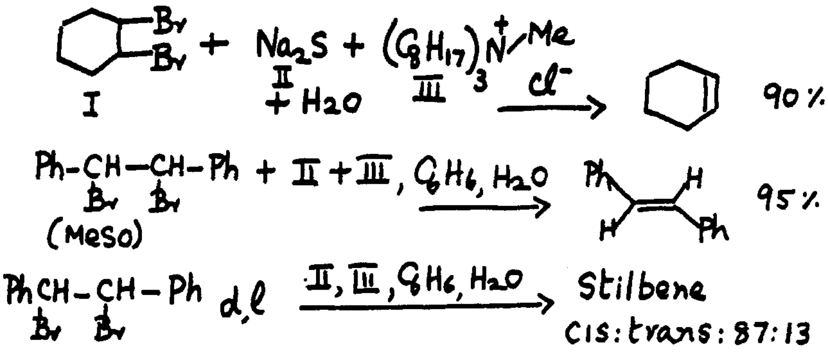
However, when the stoichiometry of the reaction is changed such that 2 moles of II react with one mole of I, then the product is the oxazolinone (IV):



IV

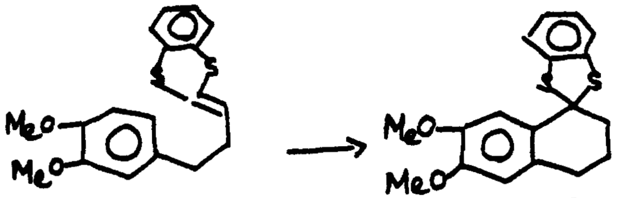
The oxazolinone was formed in high yields. That the formation of IV proceeded stepwise was confirmed by the fact that II and III react at 0° to give IV. *(Daniel M. Ketcha, Magid Abou-Gharbia, Francis X. Smith and Daniel Swern, Tetrahedron Letters, 24, 2811, 1983).*

Vicinal dibromides—a good variety of them—are readily converted to olefins by reductive **debromination using** aqueous sodium sulfide or sodium hydrosulfide. The use of **a phase-transfer catalyst** (trioctylmethylammonium chloride) in a two-phase mixture appears to be the major factor in promoting reduction over nucleophilic substitution. Some typical reactions are shown below:



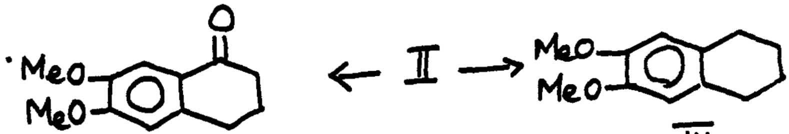
Other functional groups (like COOR or C=O) are not affected by the reagents. Stereospecific anti elimination is observed in appropriate examples cited above. The reaction is so facile that the 1,2-dibromocyclohexane reduction could be carried out in a separating funnel! This new technique commends itself as one of the best for generating olefins from vicinal dibromides. *(Juzo Nakayama, Haruki Machida and Masamoto Hoshino, Tetrahedron Letters, **24**, 3001, 1983).*

Ketenedithioacetals are shown to be particularly valuable intermediates for intramolecular **cyclization to an aromatic ring.** In the presence of *para*-toluenesulfonic acid as a catalyst, a solution of the dithioacetal (I) in dry acetonitrile undergoes ready cyclization to II, even at 0°.



I II

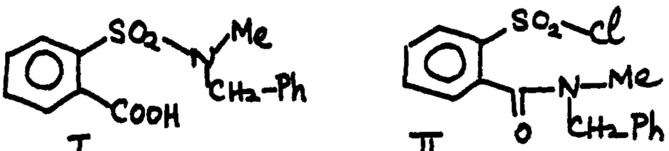
Owing to the steric bulk of the dithioacetal function, cyclization appears to occur regiospecifically, para to the methoxy group, rather than ortho. The benzodithiole (II) can be hydrolyzed to the tetralone (III) or desulfurized with Raney Ni to the tetralin (IV).



III IV

*(James H. Rigby, Atul Kotnis and James Kramer, Tetrahedron Letters, **24**, 2939, 1983).*

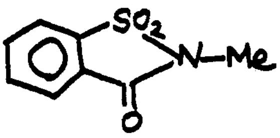
An unusual **intramolecular migration of an amine function** occurs in several ortho carboxy N,N-dialkylsulfonamides. With excess thionyl chloride in chloroform solutions, the sulfonamide I rearranges to the carboxamide II.



I II

In addition to II, N-methylsaccharin (III) and benzyl chloride (IV) were isolated in yields of 35% and 20%, respectively.

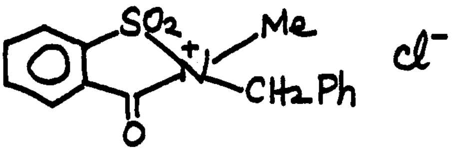
III



$Ph-CH_2-Cl$ IV

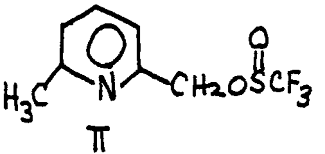
The rearrangement, it is suggested by the authors, proceeds through the intermediate V.

V

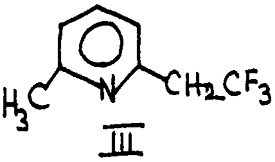


(Klaas Hovius, Anno Wagenaar and Jan B. F. N. Engberts, Tetrahedron Letters, ***24****, 3137, 1983).*

An unusual reaction between **triflic anhydride (I) and 2,6-lutidine** results in a major (II) and a minor (III) product.



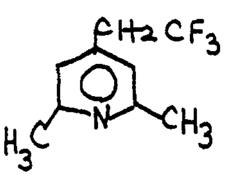
II



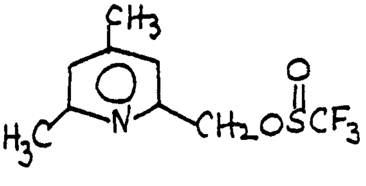
III

Similar reaction between I and *s*-collidine gives a 62% yield of IV and a 5% yield of V.

IV

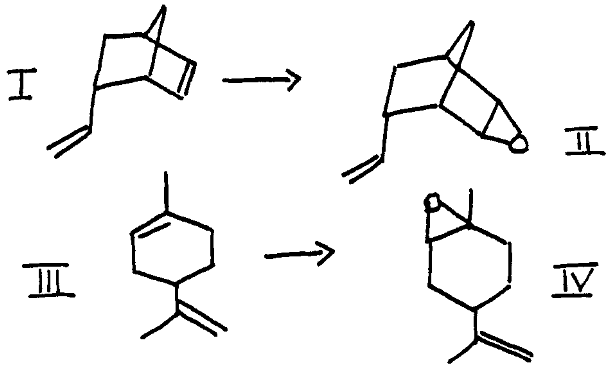


V

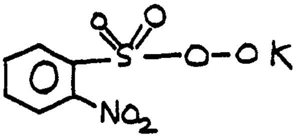


However, highly hindered bases like 2,6-di-*tert*-butyl-4-methylpyridine fail to react with I. Caution must therefore be used in employing the lutidine and collidine as base catalysts in reactions where triflic anhydride is a reagent. *(Roger W. Binkley and Michael G. Ambrose, J. Org. Chem.,* ***48****, 1776, 1983).*

A new method for the **regioselective epoxidation of olefins** is reported. The procedure uses 2-nitro-, 4-nitro-, or 2,4-dinitrobenzenesulfonyl chloride and potassium superoxide in acetonitrile solution at −35° under dry argon atmosphere. The following examples are illustrative:

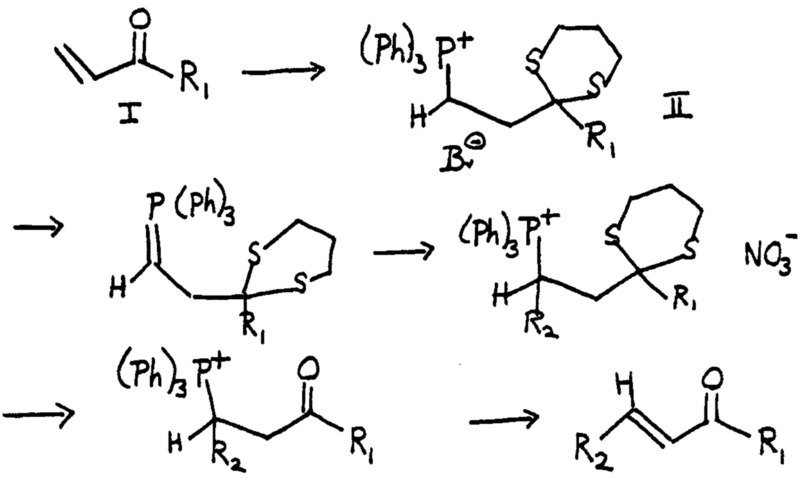


Epoxidation using 2-nitrobenzenesulfonyl chloride gave better yields of epoxides than the other two sulfonyl chlorides. The peroxysulfonate (V) is suggested to be the oxygen-transferring reactive intermediate:


V

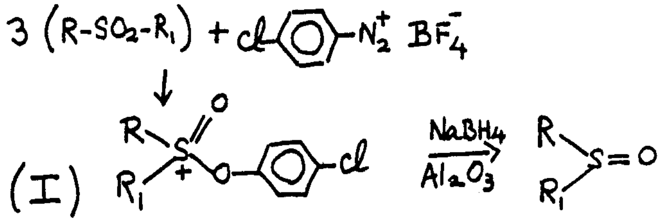
Nitrobenzenesulfonyl chlorides appear to be an essential ingredient in this epoxidation procedure. Without them, the olefins were recovered quantitatively. *(Yon Hae Kim and Bong Chul Chung, J. Org. Chem., **48**, 1564, 1983).*

A special five-step procedure is described for the selective **alkylation of α,β-ethylenic ketones at the β-carbon**. The method utilizes an electrochemical hydrolysis of the γ-thioacetalated phosphonium intermediate II, as shown below:



Electrochemical hydrolysis of the thioacetal derivative at controlled potential is a key step in this synthetic sequence. *(H. J. Cristau, B. Chabaud and C. Niangoran, J. Org. Chem., **48**, 1527, 1983).*

Sulfones are reduced to sulfoxides by the action of $NaBH_4/Al_2O_3$ on (aryloxy)sulfoxonium salts. An aromatic diazonium salt (4-chlorobenzenediazonium tetrafluoroborate is shown to work best) when decomposed in the presence of an excess of the sulfone, affords the reactive intermediate I.

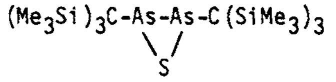


When treated with $NaBH_4/Al_2O_3$, the aryloxysulfoxonium salt gave the corresponding sulfoxide in 40 to 60% yields. By the use of $NaBD_4/Al_2O_3$, the authors show that nucleophilic hydride attack occurs at the sulfur atom of the intermediate I. *(Ian W. J. Still and Fred J. Ablenas, J. Org. Chem., **48**, 1617, 1983).*

The First Stable Diarsene: Introduction of a bulky group, namely $(Me_3Si)_3C$ serves to stabilize the first example of a stable compound with an As=As linkage in the following reaction sequence:

$$\begin{tikzcd} (Me_3Si)_3CLi+AsCl_3 \arrow[r] & (Me_3Si)_3AsCl_2 \arrow[d, dash] \\ (Me_3Si)_3C\text{-}As{=}As\text{-}C(SiMe_3)_3 & \arrow[l, "t\text{-BuLi}"'] \end{tikzcd}$$

The diarsene, purified by chromatography, is an orange crystalline solid which displays a monomeric molecular weight in solution and in the gas phase. Upon reaction with sulfur, the diarsene reacts to produce the first stable diarsathiirane whose molecular weight was confirmed by mass spectroscopy.



$$(Me_3Si)_3C\text{-}\underset{\diagdown\,S\,\diagup}{As\text{-}As}\text{-}C(SiMe_3)_3$$

*(C. Couret, J. Escudie, Y. Madaule, H. Ranaivonjatovo and J.-G. Wolf, Tetrahedron Letters, **24**, 2769, 1983).*

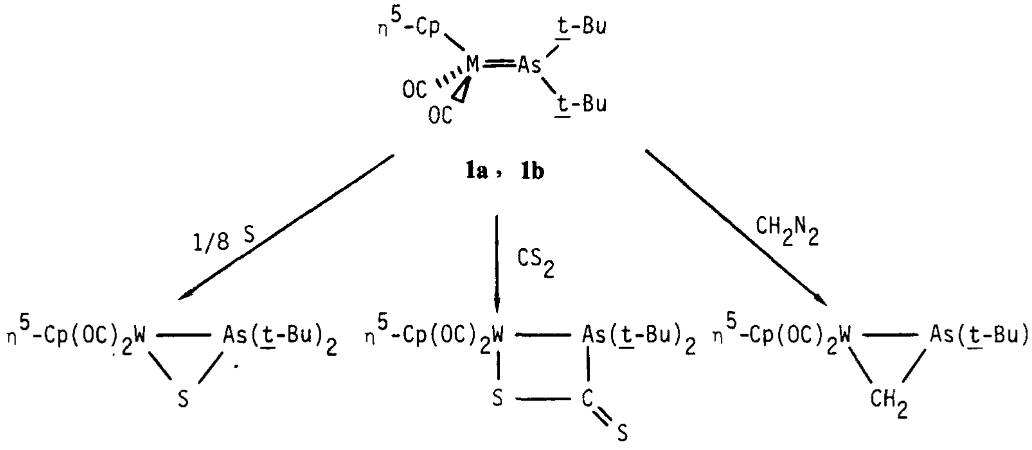
The First Metal-Arsenic Double Bond: Steric hindrance in the form of a *tert*-butyl group facilitates the remarkable transformation shown in which the first metal–

$$\eta^5\text{-Cp(OC)}_3\text{MAs}(\underline{t}\text{-Bu})_2 \xrightarrow{60^0} \eta^5\text{-Cp(OC)}_2\text{M=As}(\underline{t}\text{-Bu})_2 + \text{CO}$$

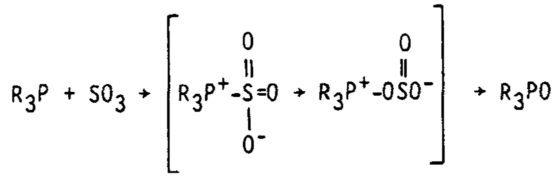
1a, M = Mo

1b, M = W

arsenic bond is stabilized. The blue **1a** and deep violet **1b** crystals are very soluble in benzene and both compounds reversibly add CO at atmospheric pressure and room temperature. The stereochemistry shown for **1a,b** below is inferred from the anisochronism of the alkyl groups in their ^{1}H nmr spectra below 45°C. Steric demands of the *t*-Bu groups favor the monomeric structure over that of a dinuclear arsenic-bridged species. The double bond nature of **1b** is manifested by its reactions shown in the scheme below. *(M. Luksza, S. Himmel and W. Malisch, Angew. Chem., 22, 416, 1983).*

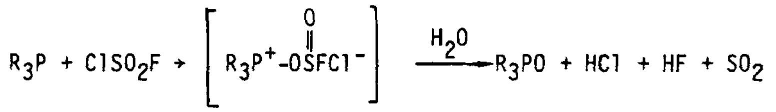


Mild Oxidation of PR$_3$ and AsR$_3$ with Ambident SO$_3$ and SO$_2$FCl: In contrast to the well-established ambident reactivity of certain nucleophiles such as CN$^-$ and NO$_2^-$, that of electrophiles is for the most part restricted to resonance-stabilized cations. Similarities in the reactivity patterns of NO$_2^+$ and SO$_3$ led to an investigation of the reaction of SO$_3$ with phosphines and arsines. Though SO$_3$ is generally considered to oxidize hydrocarbons by a free-radical process, it reacts smoothly with aryl and alkyl phosphines and arsines under mild conditions (0–25°C in CH$_2$Cl$_2$) to give the corresponding oxides in 93 to 99% yields in the case of phosphines and 70% in the case of Ph$_3$As. The mechanism is believed to be as depicted in the reaction (1).



$$R_3P + SO_3 \rightarrow \left[R_3P^+\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{S}}\text{=O} \rightarrow R_3P^+\text{-O}\overset{\overset{\displaystyle O}{\|}}{S}O^- \right] \rightarrow R_3PO \qquad (1)$$

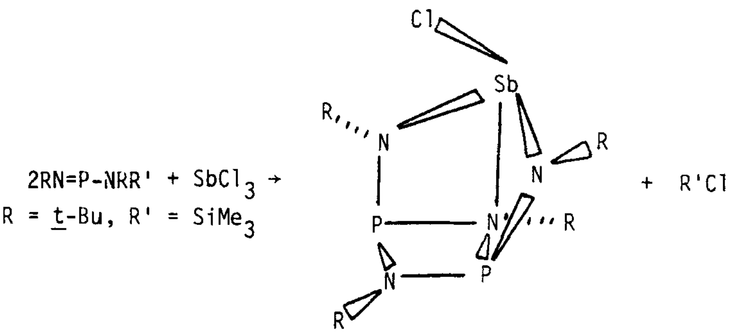
The poorly nucleophilic solvent SO$_2$ClF also readily oxidizes tertiary phosphines and arsines under mild conditions, presumably owing to the excellent leaving-group character of O_2SF. ^{31}P nmr studies indicate that R_3P attacks the oxygen atom to yield the intermediate in reaction (2).



$$R_3P + ClSO_2F \rightarrow \left[R_3P^+\text{-}O\overset{O}{\overset{\|}{S}}FCl^-\right] \xrightarrow{H_2O} R_3PO + HCl + HF + SO_2 \qquad (2)$$

(G. A. Olah, B. G. Gupta, A. Garcia-Luna and S. C. Narang, J. Org. Chem., ***48****, 1760, 1983).*

Transannular N → Sb Donation in a Bicyclic SbNP Compound: The reaction sequence below provides a new variant on reactions of this type. The bicyclic colorless product is air-sensitive and its x-ray crystallographic analysis reveals the unusual atom arrangement shown which features a planar P_2N_2 four-membered ring wherein one of the nitrogens donates a pair of electrons to the antimony. The P—N distances to this nitrogen are unusually large (1.771 (4) and 1.772(6) Å) and can therefore be considered as a model for PN single-bond lengths in trivalent phosphorus molecules. The antimony stereochemistry is a distorted trigonal bipyramid. ^1H nmr studies are consistent with the postulate that antimony inverts by an intermolecular rather than a classical intramolecular mechanism. *(O. J. Schere, G. Wolmershauser and H. Conrad, Angew. Chem., 22, 404, 1983).*



Do $Mn(RP_3)X_2$ Complexes Really Reversibly Bind O_2? The controversy surrounding the title question and the difficulties encountered with moisture contamination in preliminary experiments prompted an investigation of the $Mn(PR_3)X_2$ system under rigorously anhydrous conditions. To this end $MnBr_2$ was sublimed or sprayed in an anhydrous solvent onto a KBr infrared-cell window. The cell was then heated under vacuum until all H_2O bands vanished. From a reservoir attached to the vacuum line, anhydrous Me_3P vapor was allowed to contact the window thus forming a surface deposit of the $MnLX_2$ complex. After removing excess phosphine under vacuum, dry O_2 was placed in contact with the window and the system monitored by infrared spectroscopy. The off-white complex turned blue and bands indicative of $Mn(OPMe_3)Br_2$ as well as $Mn(PR_3)Br_2(O_2)$ were observed. The bands in the case of the latter complex are consistent with the presence of superoxide. Heating the surface produced the inactive phosphine oxide complex. Attempts to reversibly bind O_2 by exposure/evacuation cycles were not met with complete success. *(H. D. Burkett, V. F. Newberry, W. E. Hill and S. D. Worley, J. Am. Chem. Soc.,* ***105****, 4097, 1983).*

PH_2^- Reactions in the Gas Phase: In a flowing afterglow apparatus described earlier by these workers, the reaction below was used for the efficient production of PH_2^- in the gas phase:

$$e^- + NH_3 \longrightarrow NH_2^- \longrightarrow PH_2^- \qquad (1)$$

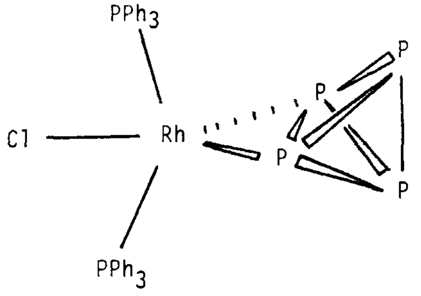
Thus NH_3 was introduced near the electron gun 135 cm upstream from the detector, PH_3 entered at 105 cm from the detector resulting in quantitative conversion to PH_2^-. Subsequent introduction of substrate gases further downstream produced known species as well as several new ones:

Substrate	Products	Substrate	Products
N_2O	PN_2^-, H_2PO^-	OCS	H_2PS^-, PCO^-, H_2PCOS^-
CO_2	$H_2PCO_2^-$	CS_2	PCS^-, $H_2PCS_2^-$, PS^-, PS_2^-
O_2	PO_2^-	NO_2	H_2P
SO_2	PSO^-, PO_2^-, $H_2PSO_2^-$	CH_3X^a	H_2PCH_3
Me_3SiCl	H_2PSiMe_3		

[a] X = Cl, Br, I

The mechanisms of these reactions are discussed in terms of proton transfer, electron transfer, nucleophilic addition and nucleophilic substitution. Although there are similarities to the reactions of NH_2^-, distinct contrasts also arise which are attributed to differences in basicity, nucleophilicity, bond strength and electron affinities. *(D. R. Anderson, V. M. Bierbaum and C. H. DePuy, J. Am. Chem. Soc.,* ***105****, 4244, 1983).*

The Structure of P_4 as a Ligand in trans-$[Rh(P_4)(PPh_3)_2Cl]$: Although a recent nmr study by one of the authors of the title complex suggested coordination of two P



atoms in the P_4 unit, the alternative η^3 coordination mode is also possible. Solutions of the complex are unstable above 260 K; however, suitable crystals (as a di-solvate) for x-ray diffraction were obtained from CH_2Cl_2 at 195 K. Accurate structural data obtained at low temperature revealed the structure depicted in which the two P atoms in the P_4 unit are bonded to the metal and are separated by an additional 0.25 Å over the normal distance in P_4 (2.21 Å). EHMO calculations led to the conclusion that both sigma and pi bonding in the observed conformation are stronger than in that wherein all the ligand atoms are in the same plane. *(E. Lindsell, K. McCullough and A. J. Welch, J. Am. Chem. Soc., **105**, 4487, 1983).*

Efficient Synthesis of Primary Amines via the Staudinger Reaction: Reductions of azides to primary amines generally pose selectivity problems and/or involve costly processes. Here the application of the Staudinger reaction to the "one-pot" high-yield (79–95%) synthesis of primary amines is disclosed. In the reaction sequence below, the primary amine is easily separated by

$$RN_3 + PPh_3 \xrightarrow[THF]{-N_2} RN{=}PPh_3 \xrightarrow{H_2O} RNH_2 + OPPh_3$$

distillation, extraction or precipitation as the hydrochloride. The mild reaction conditions tolerate the presence of other functional groups in the R substituent such as aromatic NO_2, $(EtS)_2CH$, esters, double and triple bonds and oxirane. *(H. Vaultier, N. Knouzi and R. Carrier, Tetrahedron Letters, **24**, 763, 1983).*

Origin of Unexpected Restricted Rotation in $R_3P{=}C(PR_2)_2$: The ^{31}P nmr spectra of **1** and **2** as well as the alkali-metal compounds **3** and **4** are highly temperature

$Ph_3P{=}C(PPh_2)_2$

1

$Ph_2PCH_2PhP{=}C(PPh_2)_2$

2

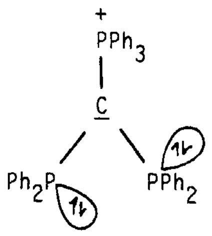
$Na^+[Ph_2PCHPh_2P{=}C(PPh_2)_2]^-$

3

$K^+[Ph_2PCHPh_2P{=}C(PPh_2)_2]^-$

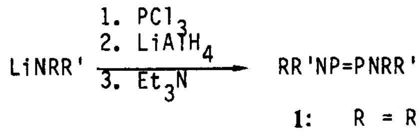
4

dependent. Above 50°C the PPh_2 phosphorus atoms attached to the ylid function are chemically equivalent whereas at −50°C they differ drastically in their chemical shifts and P—C=P coupling constants. The unsymmetrical model depicted, postulated to exist in solution, is shown to be present in the solid for **1** by x-ray



diffraction. The large differences in the P—C=P coupling constants (e.g., +173.4 and −42.7 Hz for **1**) are attributed to the "*cis*" and "*trans*" relationships of the lone pairs to the phosphorus in the PPh_3 moiety. The rotation barrier of *ca.* 50 kJ/mol is surprisingly high considering the normal P—C bond lengths. The stability of the observed conformation is attributed to the realization of minimized repulsive interactions of the phosphorus lone pairs and the sp^2 carbon lone-pair orbital which lies perpendicular to the P_3C plane. *(H. Schmidbauer, U. Deschler and B. Milewski-Mahrla, Chem. Ber., **116**, 1393, 1983).*

Structure and Bonding in $R_2NP{=}PNR_2$: The reactions below lead to the diaminodiphosphenes, of which **3** is the first unsymmetrical example.

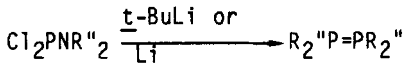


$$\text{LiNRR}' \xrightarrow[\text{3. Et}_3\text{N}]{\text{1. PCl}_3\ \ \text{2. LiAlH}_4} \text{RR}'\text{NP=PNRR}'$$

1: R = R' = $SiMe_3$

2: R = $SiMe_3$, R' = t-Bu

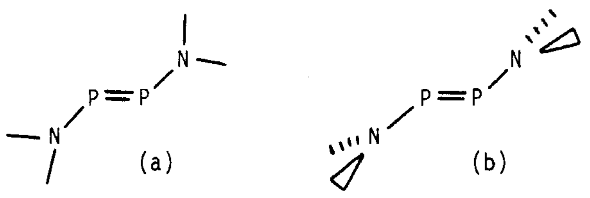
3: $(Me_3Si)_2NP{=}PN(SiMe_3)_2$



$$\text{Cl}_2\text{PNR}''_2 \xrightarrow[\text{Li}]{\text{t-BuLi or}} \text{R}_2''\text{P=PR}_2''$$

6: R'' = $SiMe_2$(t-Bu)

Whereas **1**, **2** and **3** tend to dimerize at room temperature, **6** does not. All of these products are thermochromic, turning from red at room temperature to yellow below −100°C. Substitution of Me_3Si by *t*-Bu causes the highly deshielded phosphorus resonances (*ca.* 570 ppm) to move upfield (*ca.* 70 ppm). This is tentatively rationalized on the basis of a higher population of the coplanar conformation (a)



which is calculated to have a slight preference over the bisorthogonal conformation (b). The ${}^1JPP$ value for **3** is unusually large (670 Hz) compared to a related diphosphine (148 Hz), demonstrating the influence of the phosphorus-phosphorus double bond. The structure of **6** determined by x-ray means reveals a bisorthogonal structure (b) in which the P—N distances are rather large (176.9 ppm), presumably owing to electron-pair repulsions between the bonded P and N atoms. *(E. Niecke, R. Ruger, M. Lysek, S. Pohl, and W. Schoeller, Angew. Chem., **95**, 495, 1983).*