

Designing New Molecular Metals

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Table of Contents

Introduction	page 6
Molecular metals synthesis strategy	page 7
Poly(sulfur nitride) , (SN) _x [PSN]	page 8
Bis[(phenylthio)imido]sulfurane	page 11
Bis(phenylimido)sulfurane (Cramer's synthesis)	page 12
Hydroxylamine-O-sulfonic acid	page 12
Scheme 1 : bis[(phenylthio)imido]sulfurane synthesis	page 13
Possible route to PSN via bis(imidosulfonic acid)sulfurane	page 14
Concept of the triad for Cooper pairs in superconductivity	page 15
Scheme 2 : bis[(2-methylthio)phenylimido]sulfurane	page 19
PSN analogues with the CH linkage	page 20
Bis[(phenylthio)methylidene]sulfurane	page 20
Scheme 3 : bis[(phenylthio)methylidene]sulfurane synthesis	page 21
Sulfur tetrafluoride , SF ₄	page 22
Scheme 4 : bis[(phenyl , thiomethyl)methylidene]sulfurane synthesis	page 26
Scheme 5 : bis[(2-methylthio)phenyl-methylidene]sulfurane synthesis	page 27

Scheme 6 : bis[(2-methylthio-5-methyl-phenyl)methylidene]sulfurane synthesis	page 28
A possible phosphorane molecular metal compound	page 29
Scheme 7 : bis[(N-methylphenylphosphine)imido]phenylphosphorane synthesis	page 29
Poly(methylidene)sulfurane , (CHS)_x	page 31
Scheme 8 : poly(methylidene)sulfurane , route no. 1	page 33
Scheme 9 : poly(methylidene)sulfurane , route no. 2	page 35
Poly(S-methyl-methylidene)sulfurane , (CH₃CHS)_x	page 37
Alkylidene sulfuranes	page 38
Methylthiodiazomethane	page 40
Scheme 10 : synthesis route for methylthiodiazomethane	page 42
Polymerization of methylthiodiazomethane carbene	page 43
Transition metal complexes for the polymerization catalyst	page 44
References	page 46

Illustrations

Structural formulas for poly(sulfur nitride)	page 8
Trigonal planar hybrid orbital for nitrogen in pyridine	page 9
Energy levels for s , p , d , and f native orbitals	page 10
Cramer's synthesis of bis(phenylimino)sulfurane	page 12
Kemp and Woodward's synthesis of benzisoxazole	page 12
Scheme 1 : bis[(phenylthio)imido]sulfurane synthesis	page 13
Bis[(phenylthio)imido]sulfurane(1+) tetrafluoroborate	page 15
Scheme 2 : bis[(2-methylthio)-phenylimido]sulfurane synthesis	page 19
Bis[(phenylthio)methylidene]sulfurane	page 20
Scheme 3 : bis[(phenylthio)methylidene]sulfurane synthesis	page 21
Cava and Husband's synthesis of tetraphenylthieno[3,4-c] thiophene	page 23
Bis[(phenylthio)methylidene]sulfurane(1+) tetrafluoroborate	page 24
Bis(ethylenedithio)tetrathiofulvalene , "ET"	page 25
Scheme 4 : bis[(phenyl , thiomethyl)methylidene]sulfurane synthesis	page 26
Scheme 5 : bis[(2-methylthio)phenyl-methylidene]sulfurane synthesis	page 27

- Scheme 6 : bis[(2-methylthio-5-methyl-phenyl)methylidene]
sulfurane synthesis [page 28](#)
- Scheme 7 : bis[N-(methylphenylphosphine)imido]phenylphosphorane
synthesis [page 29](#)
- Phosphorus(V) trigonal planar , phosphorus(III) tetrahedral
hybrid orbitals [page 30](#)
- Poly(methylidene)sulfurane structural formula [page 32](#)
- Scheme 8 : poly(methylidene)sulfurane synthesis , route no. 1 [page 33](#)
- Ingold and Jessop's synthesis of dimethyl-9-fluorenyl sulfonium
bromide [page 34](#)
- Scheme 9 : poly(methylidene)sulfurane synthesis , route no. 2 [page 35](#)
- Moody and Taylor's synthesis of 2-carbomethoxy-3-thia-
S-ethyl-cyclohexanone betaine [page 37](#)
- Ando's synthesis of dimethyl (2-dimethylsulfonium)malonate
betaine [page 38](#)
- Sketch of the orbitals for $(\text{CH}_3)_2\text{S}^+ \rightarrow \text{CH}_2$ (betaine form) [page 39](#)
- Poly(S-methyl-methylidene)sulfurane , betaine form [page 40](#)
- Poly(S-methyl-methylidene)sulfurane , metallic form [page 41](#)
- Scheme 10 : methylthiodiazomethane synthesis [page 42](#)
- Polymerization of methylthiodiazomethane to $(\text{CH}_3 - \text{S}=\text{CH})_x$ [page 43](#)

Designing New Molecular Metals

Introduction

How do you approach the synthesis of new metallic solids ? We are all familiar with the common metals around us . Nature has provided about seventy metallic elements and a half dozen or so semi-metals as well . There are also the alloys and intermetallic compounds of these elementary metals . However , the metallic bond is one of the five fundamental types of chemical bonds that can be present in matter . As such , it can theoretically occur in many different sorts of crystalline solids (I am disregarding in this report liquid and glassy metals) . It can be found in molecular solids , nonmolecular solids (infinite or extended atomic lattices) , and in macromolecular or polymeric compounds . The actual chemical technique required by the researcher to synthesize a new metallic solid will depend on the general sort of chemical system in which the target material is classed : molecular , lattice , or polymer .

What is clear at the outset is that the investigator must understand several things about the particular chosen system . First , the atomic structure of the component molecules , macromolecules , or lattice must be known . Then , the chemical bonds present in the crystal must be described . Third , the electronic structure of the atoms contributing valence electrons to the metallic bond must be determined . With this information in hand , the metallic bond in the material can be analyzed and understood . Only then can a rational approach to the design and synthesis of specific target molecules , macromolecules , or lattices be reasonably undertaken .

In a previous report , “Exploring the Chemistry of Metallic Solids , Including Superconductors” , many metallic solids , both known and proposed , were described and discussed . The nature of the metallic bond was studied in general , and in the specific cases chosen as educational and revealing to researchers . While this report was concerned mostly with

lattice compounds , several interesting molecular and macromolecular metallic solids were also briefly examined .

In this present report , my objective will be to extend our examination of the metallic bond in **molecular solids** , illustrating the theoretical concepts with what I hope are vivid , thought-provoking examples of possible new molecular metals . The chemical methodology employed in this second study is that of organic chemistry , contrasting with the inorganic chemistry of the first book about metallic solids . That is one reason I chose to exclude this report from the previous work , which in any event was judged long enough . However , the interested reader should refer to the “Exploring” book for a detailed discussion of the theory and description of the metallic bond in a wide range of materials .

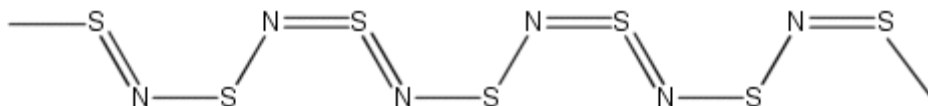
Molecular metals synthesis strategy

First , I should distinguish between the two terms , “molecular metal” and “synthetic metal” [synmet] . The former material is composed of discrete molecules as the structural unit , which in turn are essentially organic compounds **not** containing any metal atoms . The latter material is also composed of molecules , but contains one or more metal atoms per unit formula . The metal atoms are often bonded to the organic ligands by coordinate covalent bonds . Also , the metallic bond in synthetic metals is derived from valence electrons in the metal atom component .

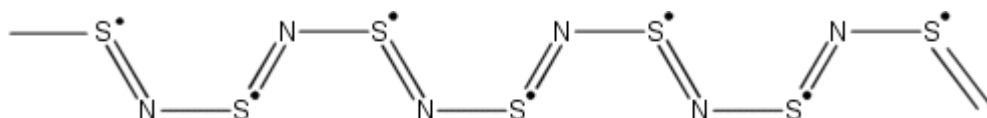
In molecular metals , the commonest atom providing the free electrons in the metallic bond is the **sulfur** atom . True , a number of molecular metals with selenium as the “active” atom are known – for example the organic superconductor $(\text{TMTSF})_2\text{ClO}_4$ – but the sulfur-based molecular metals are better known and their chemistry base is wider and more familiar than that of the heavier chalcogenide elements , selenium and tellurium . Only sulfur compounds will be discussed in this report .

The macromolecular compound poly(sulfur nitride) , $(\text{SN})_x$ [which I abbreviate PSN] , was studied in the “Exploring” book . It will be helpful to briefly review the nature of the metallic bond in PSN , since an understanding of it will provide the synthesis rationale for other sulfur-based molecular metals .

PSN consists of long chains of alternating sulfur and nitrogen atoms , linked together in a crenellated (“all-Z”) pattern :

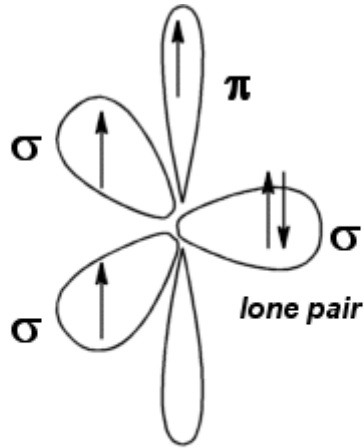


Note carefully that bonding in the sulfurs alternates from divalent to tetravalent in this “organic chemistry” structural formula of the compound . However , it seems that resonance occurs spontaneously in the chains , so as to create a continuous pi bond “cloud” over their entire length :



The first structure above would represent the **disproportionated** form , in which the pi electrons are localized ; in the second form , they are resonating and delocalized in the pi cloud . Both the nitrogen and sulfur atoms in this latter **reproporionated** form of PSN have an electronic structure similar to that of the nitrogen atom in the pyridine molecule , for example (see the sketch at the top of the following page) . This trigonal planar $sp^2 + 2p_z$ hybrid orbital can accommodate five valence electrons , which is suitable for the nitrogen atoms . Sulfur , though , has **six** valence electrons ($3s^2 3p^4$) ; where will the “sixth” electron go ?

As explained in the “Exploring” book , the physical and chemical properties of PSN suggest that it may have been promoted into the 4s **frontier orbital** over the sulfur atom , possibly with some resonance into the N 2p – S 3p pi* ABMO , (ref. 1 , [page 46](#)) ; PSN is somewhat unstable , and detonates when mechanically compressed , or heated to about 240 °C . The 4s orbitals , with

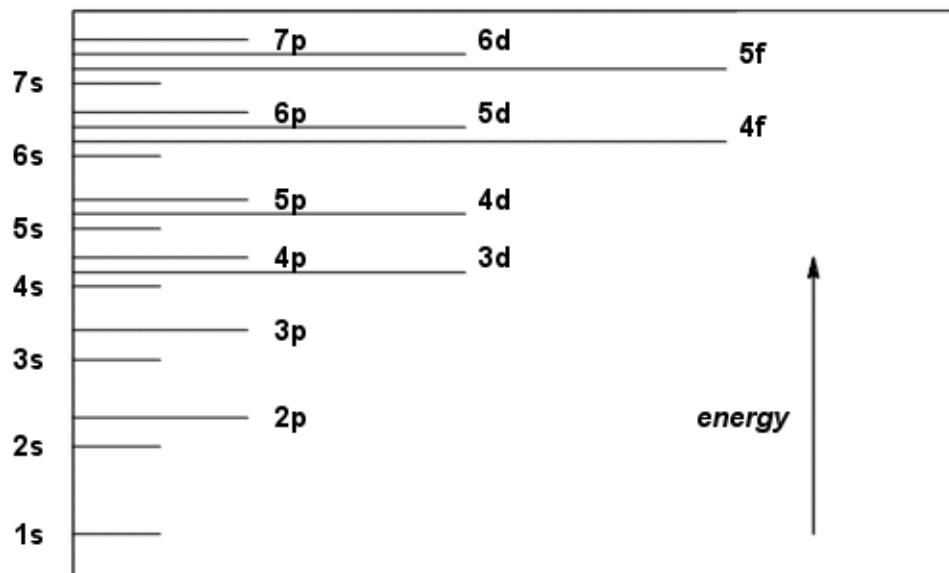


**$sp^2 + 2p_z$ trigonal planar hybrid orbital
in pyridine's nitrogen atom**

their “sixth” valence electrons from the sulfurs , can overlap continuously along the chains to form the **nodeless** sigma XO , which is the proposed metallic bond in poly(sulfur nitride) .

PSN really represents a form of **metallic sulfur** , since the 4s sigma XO is expected to extend over and between the sulfur atoms , and avoid the nitrogen atoms . This is because of the rather large energy gap between the 2 s-p energy level of the nitrogen valence shell electrons , and the 4 s-p energy level of the S-S metallic bond (see the sketch of the energy levels of the s , p , d , and f orbitals at the top of the following page) . A free electron in the sigma XO will be energetically destabilized when approaching a nitrogen atom because of the level “mismatch” , and so will tend to be confined to the sulfur atoms’ interatomic volume . This same argument can be applied to other molecular metals based on electronically active sulfur atoms . The surrounding hydrocarbon framework is really just that : an electronically inert skeleton .

Three types of bonds can be distinguished in PSN : two covalent bonds , the low energy localized sigma and medium energy resonant pi MOs ; and the higher energy delocalized metallic bond , the sigma XO . These all seem



to be rather feeble , for as noted , poly(sulfur nitride) is mechanically and thermally unstable , as are most if not all sulfur-nitrogen compounds .

The above considerations suggest that in order to design and synthesize new PSN analogue molecular metals , we must devise a way to obtain the unnatural “metallic” sulfur(III) valence state in the candidate compounds , in which the sulfur “sixth” valence electrons are promoted up above the covalent skeleton into the 4s frontier orbitals . We might in turn obtain the sulfur(III) valence state – or possibly even a **non-integral oxidation state (NIOS)** valence for the sulfurs – by the **reproportionation** (chemical “blending”) of the two common valence states for sulfur , II and IV . The third sulfur valence state , VI , seems to be inapplicable , as sulfur atoms in such a valence state are either tetrahedral (eg. sulfate anion) or octahedral (eg. hexafluorophosphate anion) in coordination . For the preparation of new molecular metals , we need the sulfur(III) atoms in a **trigonal planar** coordination by other atoms , as they are in PSN .

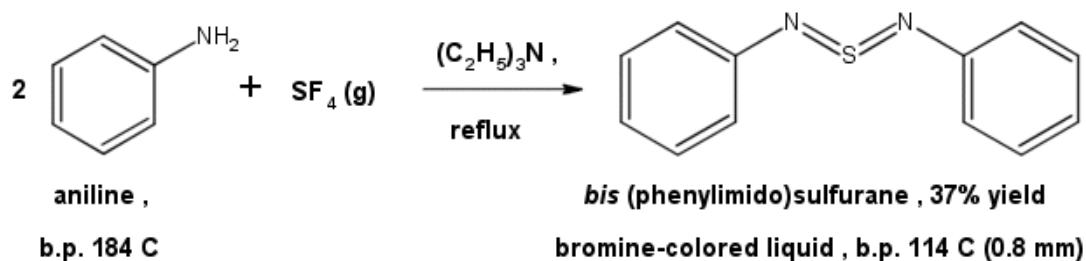
Sulfur(II) covalent compounds are well known , such as the organic sulfides [thioethers] . The sulfur atoms in these molecules have a tetrahedral

configuration , with two sigma covalent bonds and two non-bonding lone pairs of electrons . However , they can readily re-hybridize to a trigonal planar configuration when forming a resonance-stabilized system with the sulfur(IV) atoms , and the metallic bond , of course .

The sulfur(IV) compounds are less well known and accessible than sulfur(II) containing molecules . Several examples of common sulfur(IV) compounds include the industrial pollutant gas sulfur dioxide , the organic synthesis reagent thionyl chloride , SOCl_2 , and the highly toxic fluorinating agent **sulfur tetrafluoride** , SF_4 , which will be the key sulfur(IV) chemical and **synthon** , or molecular building block , in the reaction schemes I'll be proposing later .

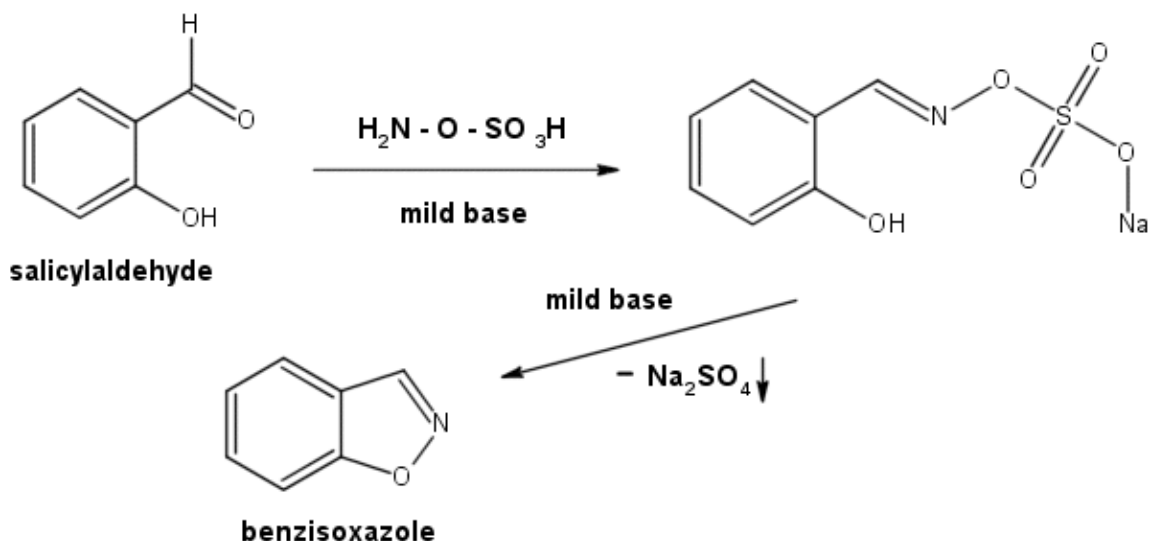
I am unaware of any common **organic** molecules containing sulfur(IV) , so I will suggest new reaction routes to these novel compounds . If we can include sulfur(II) atoms in these sulfur(IV) containing molecules , and ensure that they can be repropportionated by resonance , we should be able to produce the metallic sulfur(III) – or NIOS – valence state in the material . It should then exhibit metallic properties , as does PSN . As a bonus , it might even be a **superconductor** , albeit at a very low temperature close to absolute zero ; for , as pointed out in the “Exploring” book , PSN and its molecular metal analogues have been assigned to Class 2 of the metallic solids categories , and are grouped in the less formally defined general type of metallic solids , the **bronze metals** . These materials are all excellent ambient electrical conductors , but are well known to have extremely low superconductor transition temperatures , if any .

The electronically active part of PSN is the atomic grouping $-\text{S}-\text{N}=\text{S}=\text{N}-$; can we incorporate this group into a molecule , rather than in a polymer ? To make the group symmetrical , we'll add another sulfur atom to the right hand side , and cap the ends with phenyl groups , to obtain the hypothetical molecule $\text{Ph}-\text{S}-\text{N}=\text{S}=\text{N}-\text{S}-\text{Ph}$. The symmetry of the target molecule is very helpful , since we can react two $\text{R}-\text{NH}_2$ molecules with the highly electrophilic SF_4 to obtain the desired $\text{R}-\text{N}=\text{S}=\text{N}-\text{R}$ functionality . An example of this sort of reaction is that one between aniline , $\text{Ph}-\text{NH}_2$, and SF_4 (ref. 2 , [page 46](#)) :



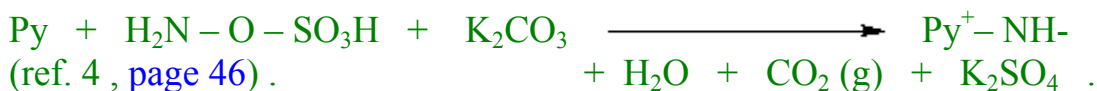
In the examples in this work , I refer to the sulfur(II) functionality in $\text{R} - \text{S} - \text{R}^*$ (sulfides , thioethers) , as “thio” , and to the sulfur(IV) functionality in $\text{X} = \text{S} = \text{X}$ as “sulfurane” . In phosphorus analogues (page 29) , the $\text{X} - \text{P} (\text{R}) - \text{X}$ phosphorus(III) is “phosphine” , and the $\text{X} = \text{P} (\text{R}) = \text{X}$ phosphorus(V) is “phosphorane” . Sulfur tetrafluoride could be called tetrafluorosulfurane , I suppose .

A key component in the synthesis scheme for the PSN molecular analogue is the well-known reagent , **hydroxylamine-O-sulfonic acid** , $\text{H}_2\text{N} - \text{O} - \text{SO}_3\text{H}$. It has two useful functionalities for our reaction . First , its amino group is basic and nucleophilic (in basic media) , and should readily condense with the electrophilic SF_4 , as aniline did . Second , its sulfonic acid group is labile , and can be displaced from the nitrogen atom by even relatively weak nucleophiles . These reactions are illustrated in the following example :

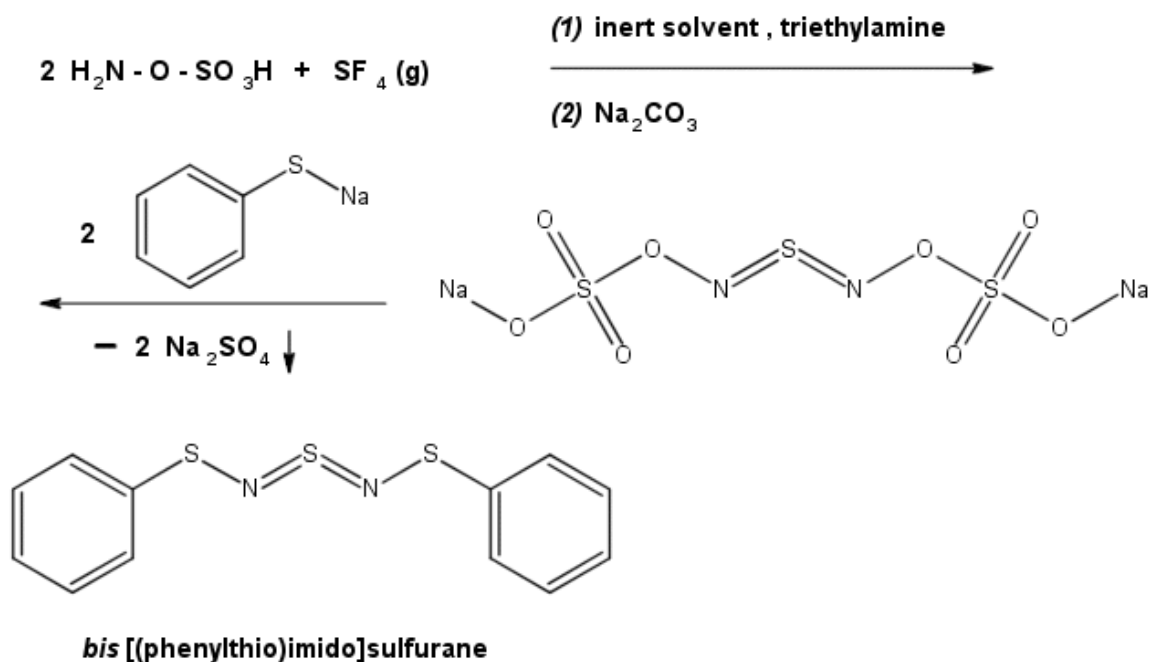


(ref. 3 , page 46) .

A second example , difficult to draw with my chemistry software , is the reaction of pyridine , “Py” , with hydroxylamine-O-sulfonic acid :



The following synthesis route in scheme 1 is proposed for the preparation of the PSN molecular analogue , bis[(phenylthio)imido]sulfurane :

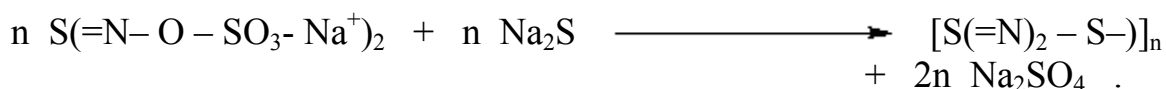


I can't seem to draw ionic structures such as R – O- Na⁺ with my chemistry software , and so must represent them with the misleading covalent bond , such as R – O – Na . My apologies !

Hydroxylamine-O-sulfonic acid is condensed with sulfur tetrafluoride in the presence of a mild base such as triethylamine (to scavenge the by-product HF) . This should provide the valuable intermediate compound , bis(imido sulfuric acid)sulfurane as the sodium salt after neutralization with base .

The sulfonic acid groups in this compound should be labile to nucleophilic displacement, and reaction of the sodium salt of the sulfurane with the sodium salt of thiophenol will hopefully provide a good yield of the desired PSN molecular analogue compound, bis[(phenylthio)imido]sulfurane. If resonance doesn't spontaneously occur in this compound to provide the repropportionated sulfur(III) metallic material, it could be subjected to one-electron oxidation, either in the anolyte of an **electrocrystallization cell**, or with a one-electron oxidizer, such as a **nitrosonium salt** (for example), $\text{NO}^+ \text{X}^-$, where X^- is an inert anion such as BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , or ClO_4^- . These are crystalline, commercially-available reagents; the nitrosonium cation is a moderately strong oxidizer at 1.45 V to $\text{NO}(\text{g})$. Partial one-electron oxidation of the sulfurane (on one of the "thio" sulfur atoms) would surely induce resonance over the entire molecule, and in doing so would cause the remaining two "sixth" valence electrons on the sulfurs – now equivalent – to be promoted up into the 4s frontier orbitals. When the partially oxidized compound crystallizes, it should form metallic crystals from the reaction solution.

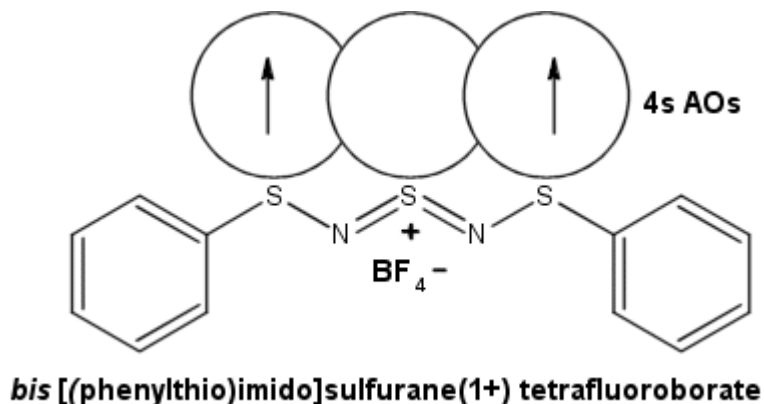
The reaction illustrated for thiophenol could be a general one for a wide range of thiols (mercaptans). In fact, **sodium sulfide** might react with the sulfurane intermediate to produce poly(sulfur nitride):



To help induce the formation of long, acicular needles of product, a **crystal habit modifier** could be added to the aqueous (or other) solution of the reagents. A **surfactant (detergent)** such as "Teepol" has been used in the crystallization of fibrous crystals from solution (ref. 5, page 46). The detergent might also suppress the formation of low molecular weight oligomers such as tetrasulfur tetranitride, S_4N_4 , in this latter reaction.

There is a rather intriguing aspect to the one-electron oxidation of these proposed PSN molecular analogues. Suppose we were to combine equimolar quantities of the analogue and a suitable one-electron oxidizer such as the moderately strong oxidizer, nitrosonium tetrafluoroborate,

$\text{NO}^+ \text{BF}_4^-$, a stable crystalline salt (commercially available, eg. from Alfa Aesar, Aldrich Chemicals, etc.). A reasonably inert solvent would have to be found for both the analogue compound and the nitrosonium salt (possibly propylene carbonate, which has a remarkably high dielectric constant (65.1) and dipole moment (4.98 debyes); b.p. 240 °C. It has been used effectively in electrochemical research, and will even dissolve inorganic salts to a certain extent; ref. 6, page 46). The analogue compound, bis[(phenylthio)imido]sulfurane, has three sulfur atoms that will be isoelectronic after reproporationation and pi MO resonance. The oxidizer will remove one of the “sixth” valence electrons, probably from one of the sulfur(II) “thio” atoms. After reproporationation, the “sixth” electrons on the other two sulfur atoms will be promoted up into the 4s frontier orbitals. These might be able to overlap continuously in the crystallized oxidized product to form a sigma XO metallic bond, and make the material metallic:



What really makes this interesting (to me, anyway) is that we have a **triad** of sulfur atoms **contained in a single molecule**. The concept of the triad as a unit for generating **Cooper pairs** of electrons – the charge and energy carriers in superconductors – was discussed in the “Exploring” book. A triad of copper cations occurs in the unit formula of the famous high temperature superconductor, “YBCO” ($T_c = 93 \text{ K}$), which has the idealized empirical formula $\text{YBa}_2\text{Cu}_3\text{O}_7$. We can write out the detailed “valence-counting” formula of YBCO as follows: $(\text{Y}^{3+}\text{Ba}^{2+}\text{Ba}^{2+})(\text{Cu}^{2+}\text{Cu}^{3+}\text{Cu}^{2+})\text{O}_7^{14-}$. The copper triad, which is the electronically active part of the compound, has a **diamagnetic base** of copper(III) cations, with **two** “ninth” valence electrons

from the formally copper(II) cations , promoted up into the $4p_z$ frontier orbitals : $(\text{Cu}^{2+}\text{Cu}^{3+}\text{Cu}^{2+}) \rightarrow (\text{Cu}^{3+}\text{Cu}^{3+}\text{Cu}^{3+} + 2e^-)$. It is these two promoted electrons that , together with participation from the intervening oxides anions ($2p_z^2$ valence electrons) , create the pi XO metallic bond in YBCO . It is also those two copper (II) “ninth” valence electrons that couple together in the superconducting state to create its Cooper pairs .

It is also the “hole” in the copper triad , caused by the formally copper(III) atom in it , that permits YBCO to function as a metallic solid in the first place . The material is a Robin-Day Class II mixed-valent compound (ref. 7 , [page 46](#)) , with a reproporationation of the formally (II) and (III) valences to the NIOS valence $2.33+$. The copper(II) ‘ninth’ electrons are able to rapidly exchange with neighboring copper atoms , thus activating the metallic bond in the lattice . YBCO is a **true metal** , having an inverse temperature – electrical conductivity relationship . Its ambient electrical conductivity is about $500 \text{ ohm}^{-1} \text{ cm}^{-1}$, typical of the “ceramic” superconductors .

By analogy , then , the partially-oxidized tetrafluoroborate salt of the PSN analogue would also be a mixed-valent compound , but this time it should be classified as Robin-Day Class IIIB , a molecular metal , since the metallic bond over and around the sulfur atoms doesn’t involve either the hydrocarbon framework of the molecule , nor the inert BF_4^- anions . I would place it in Class 4 of the general classification of metallic solids I introduced in the “Exploring” book . As you can see in the sketch of the partially oxidized molecule above , there is now a “hole” in the triad of sulfur $4s$ “sixth” electrons . Will this function in the same manner as the copper cation triad in YBCO does ?

Perhaps not . Remember , molecular metals are bronze metals , whose superconducting members always have extremely low transition temperatures , generally in the $0 - 25 \text{ K}$ range . As discussed in the “Exploring” book , there are three reasons for this .

First , the metallic bond in them is a **monolayer** , not involving any anion contribution , which would make it **bilayer** , as in YBCO and other high

temperature superconductors . The valence electrons in monolayer metallic bonds are subject to the **Fermi-Dirac distribution** , after which only a small percentage of them (perhaps 1% or so) remain above the **Fermi level** and are able to contribute to the metallic properties of the solid . It is hypothesized that in the bilayer metallic bonds , the relatively high energy copper “ninth” electrons “float” in the upper layer above the lower energy anion valence electrons ; the Fermi layer occurs at the boundary between the two layers , resulting in a very rich population of free electrons in the upper layer .

Second , in the monolayer metallic bond , the free electrons will on average be quite widely separated in the crystal’s physical dimensions . This will make them very difficult to couple together into Cooper pairs (by whatever mechanism ; and I have proposed a very simple , straightforward magnetic force coupling mechanism in the “Exploring” book) . On the other hand , in the bilayer metallic bonds , **neighboring** free electrons will be able to couple together at a much shorter distance than those in monolayer metallic bonds . It will be easier to form Cooper pairs in them , and they will be more strongly bound together and more thermally stable than the those Cooper pairs in the bronze metals .

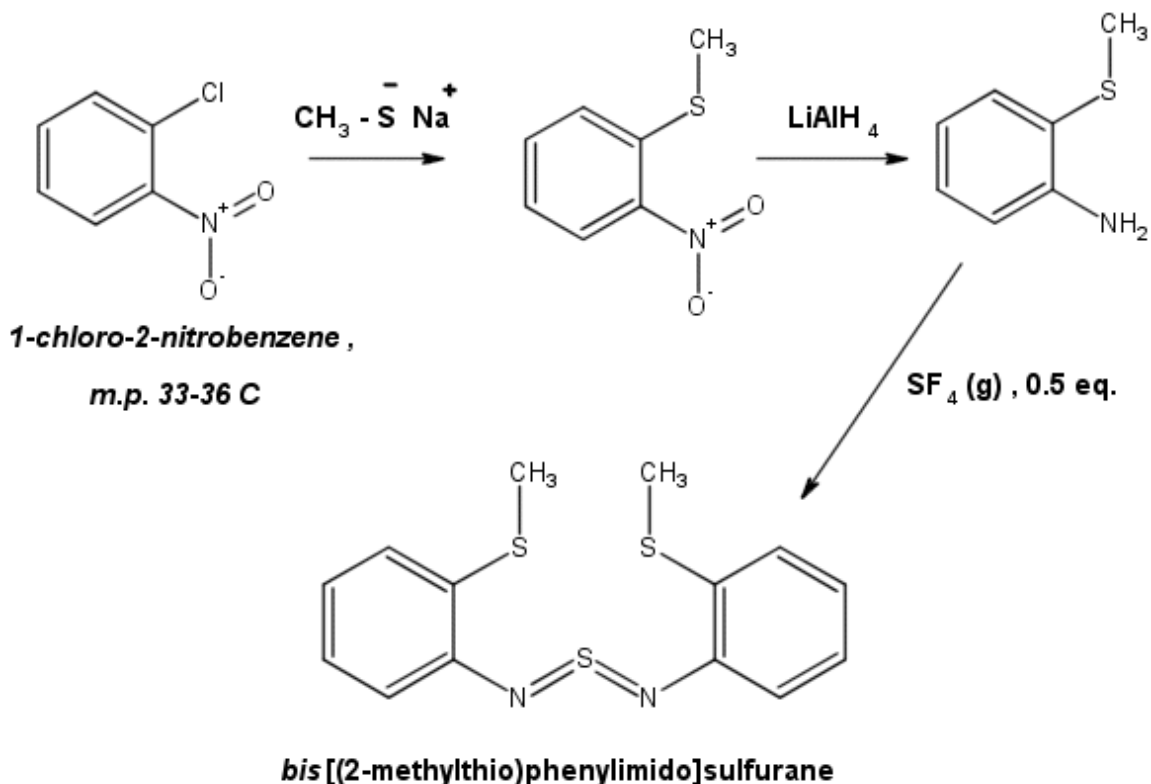
Third , it is again hypothesized that in the bronze metals the free electrons have a predominately **parallel** spin orientation , and tend to resonate **vertically** when the crystal receives energy (heat , light) from the environment . That is , the free electrons rise and fall in the vast number of energy levels comprising the metallic bond . This contrasts with the predominately **antiparallel** spin orientation of the free electrons in the bilayer metallic bonds of the **black metals** , as I have referred to them . The black metals have been derived from **antiferromagnetic precursor lattice compounds** , and the antiferromagnetism has been conferred upon the free electrons in the bilayer metallic bond in them . As mentioned , the free electrons in the mixed-valent compounds (Robin-Day Class II , or generally Class 3) tend to resonate **horizontally** , from atom to atom , and not vertically (up and down in the energy levels of the XO) . The antiferromagnetic antiparallel ordering of the free electrons , and their horizontal resonance , are of vital importance in assisting in the easy formation of the Cooper pairs at relatively elevated temperatures . These

features are obviously missing in the bronze metals ; hence their extremely low transition temperatures , if any , as superconductors . Some metals , like copper , silver , and gold (which are “bronze metals”) , while being excellent electrical conductors over a wide temperature range , never become superconducting at any temperature .

The partially-oxidized tetrafluoroborate salt molecule shown on [page 15](#) is very interesting in that the triad is contained within the molecule itself , in contrast with the existing sulfur-based molecular metals , in which the triad must form in between different molecules . In other words , our analogue salt molecule candidate could have **intramolecular** Cooper pairs , compared to the conventional molecular metals , with **intermolecular** Cooper pairs . Would this make a significant difference in its transition temperature , assuming it actually became superconducting near absolute zero ? It might help a little bit !

Even more interesting is the possibility of cramming the three sulfur atoms together as closely as possible in the candidate molecule , since the closer the free electrons are physically , the more easily they can couple together . A second factor then comes into play : the **orbital symmetry** of the component XO orbitals . Will the 4s AOs all have the same symmetry properties , thus imparting an undesirable parallel orientation to the free electrons in them ? That would make the material a bronze metal with a monolayer metallic bond , as expected . If we were somehow able to design the molecule so as to impart an antiparallel orientation into the two remaining sulfur “sixth” electrons in the 4s AOs , **and** if the three sulfur atoms in the molecule were arranged in close proximity to each other , we might then be able to significantly enhance the transition temperature of the PSN analogue candidate compound . However , a sobering reminder : the material will always remain a bronze metal , so realistically we shouldn't expect its transition temperature to exceed 25 K or so .

The creative organic chemist will delight in designing variations of the PSN analogue molecule , and in devising synthesis schemes for the variants . For example , the following scheme 2 is outlined on the next page as a possible route to another molecular metal candidate compound :



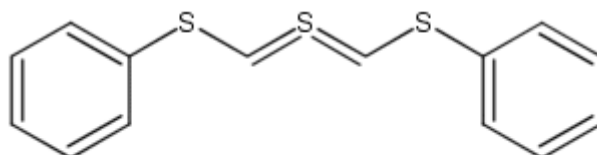
The starting material , 1-chloro-2-nitrobenzene , is a readily available , relatively inexpensive organic chemical (Aldrich Chemical Co.) . The nitro group “beta” to the chlorine atom makes the C–Cl bond labile and the chlorine susceptible to nucleophilic displacement . The 2-methylthioaniline should react with sulfur tetrafluoride in a manner similar to that of aniline itself , as illustrated above on [page 12](#) (although I hope the researcher can improve the yield somewhat over the rather low 37% obtained by Cramer) . If the molecule has the geometry shown in the sketch , the three sulfur atoms are now in a tighter cluster than in the analogue BF_4^- - salt structure shown on [page 15](#) . The 4s AOs on the sulfurs will have a much more extensive overlapping than in it as well , forming a dense sigma cloud in the molecule’s central “cavity” . How this will affect the electronic and electrical conductivity properties of the compound , especially of its partially oxidized , mixed-valent , Class 4 BF_4^- salt , remains to be determined experimentally . Perhaps other researchers can devise and create yet more unique variations of this PSN analogue molecular system .

PSN analogues with the CH linkage

MacDiarmid et al. (cited in ref. 1 , page 3 , [page 46](#)) pointed out that ,

“..... (HCS)_x – and its derivatives (RCS)_x , if they could be synthesized – might be expected to be metals” (their p. 71) .

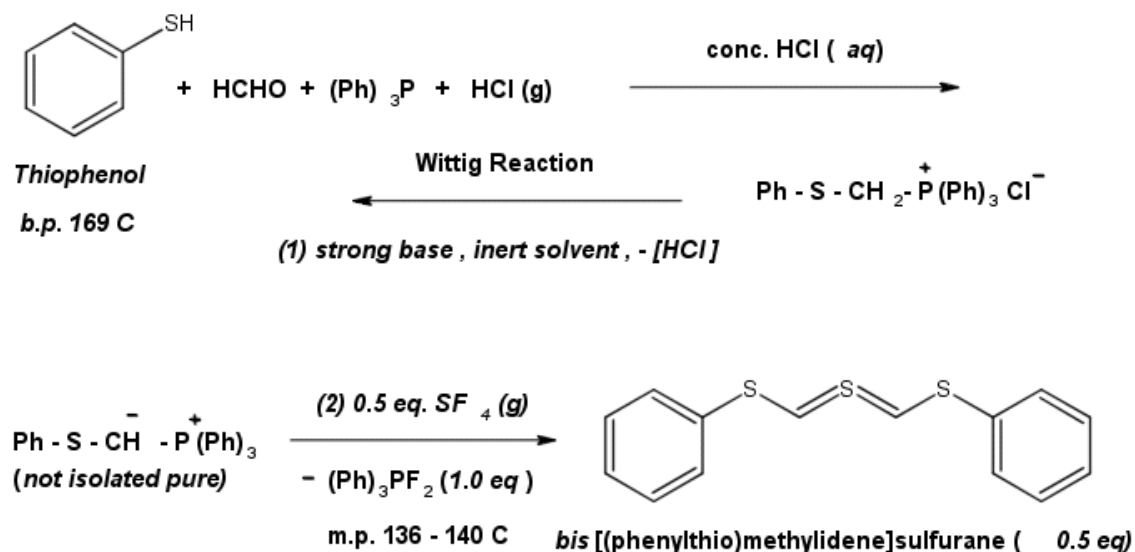
In these examples , CH and CR are replacing the inert nitrogen atom linkage in poly(sulfur nitride) . The “CH replacement molecule” for the PSN molecular metal analogue , bis[(phenylthio)imido]sulfurane , would then be bis[(phenylthio)methylidene]sulfurane , where “CH” (methylidene) replaces “N” (imido) :



bis [(phenylthio)methylidene]sulfurane

The synthesis strategy for this new molecule will be the reaction of a nucleophilic center with the highly electrophilic sulfur tetrafluoride . Such a strong nucleophile might be a **Wittig reagent** , $R - C^-(R^*) - P^+Ph_3$; in our case , $R^* = H$. The Wittig reagent required for reaction with SF_4 to produce the target molecule will then be $Ph - S - CH^- - P^+Ph_3$, obtained from the reaction of $Ph - S - CH_2 - Cl$ with triphenylphosphine . In turn , the chloromethyl phenyl sulfide can be prepared from the condensation of thiophenol , formaldehyde , and hydrogen chloride gas and acid [**this chemical is also commercially available , eg. from the Aldrich Chemical Company**] . Possibly the formaldehyde and HCl could be “pre-reacted” with triphenylphosphine to yield the known compound $Ph_3P^+ - CH_2OH Cl^-$, which is subsequently condensed with thiophenol . A suggested reaction sequence for the synthesis of bis[(phenylthio)methylidene]sulfurane is outlined in scheme 3 on the next page . Clearly , several variations of this route to the sulfurane are possible , and could be investigated by researchers

in order to optimize the yield of the PSN CH molecular analogue :



It does seem possible to prepare a Wittig reagent from an α -chlorosulfide ; at least , one has been prepared from chloromethyl methyl ether , via the phosphonium salt , CH₃ - O - CH₂ - P⁺Ph₃ Cl⁻ (ref. 8 , [page 47](#)) .

The by-product , difluorotriphenylphosphorane , described as a colorless , crystalline solid , m.p. 136-140 °C (ref. 9 , [page 47](#)) , might be a nuisance to separate from the desired sulfurane . Fractional crystallization or column chromatography might have to be resorted to . On the other hand , if the pi MO system forms spontaneously by repropotionation in the sulfurane , the sulfurane might crystallize directly from the reaction solvent in metallic needles or spars , excluding the by-products . The difluorophosphorane is the fluorine equivalent of triphenylphosphine oxide , the usual by-product in the conventional reaction of Wittig reagents with aldehydes and ketones .

Speaking of which , I couldn't find a reference to the reaction of Wittig reagents with sulfur tetrafluoride in [Chemical Abstracts](#) , although I did notice an interesting synthesis of the **sulfine** functionality , R(R*)C=S=O , from the reaction of a Wittig reagent with **sulfur dioxide** (ref. 10 , [page 47](#)) . Would the reaction of **two** equivalents of Wittig reagent with **one** equivalent

of sulfur dioxide produce a sulfurane ? An even simpler experimental variation of this theme would be the reaction of **thionyl chloride**, SOCl_2 , b.p. $79\text{ }^\circ\text{C}$ and a common, inexpensive organic synthesis chemical, with a Wittig reagent in a 1 : 2 ratio to produce a sulfurane.

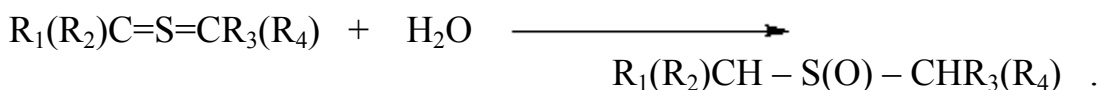
Both sulfur dioxide and thionyl chloride would be simple, cheap alternatives to the rather awful sulfur tetrafluoride, a highly toxic, corrosive gas (SO_2 and SOCl_2 are only slightly less unpleasant chemicals to work with). The interested reader who would like to investigate these reactions with SF_4 should carefully consult the reference literature concerning the safe handling and properties of sulfur tetrafluoride. Two chemical companies (I am aware of) offer commercial quantities of SF_4 (94% purity): Air Products and Matheson Tri-Gas. They provide on-line (and possibly also printed) technical brochures on their SF_4 gas products on these Web pages:

<http://www.airproducts.com/Products/Chemicals/Fluorination/sulfur.htm>,
and,
<http://www.matheson-trigas.com/mathportal/> (which is their home page; then follow the appropriate links to the brochure).

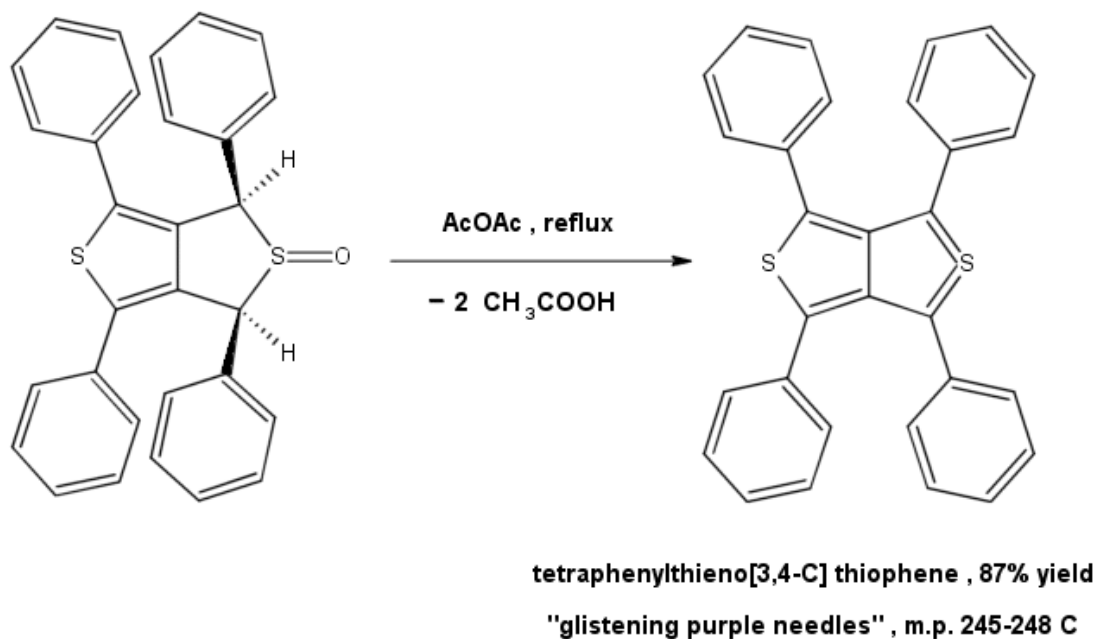
I cannot overemphasize the great need for **safety** if the following procedures – and any others mentioned in this text – are carried out. The reader must assume full responsibility for the safe manipulation of the reagents cited and in carrying out any actual trial runs. Of course, I expect all my readers are mature, responsible chemists, and are well versed in chemical theory and practice. As a basic minimum precaution, however, I would suggest that no more than semi-micro quantities of reagents (a gram or less) be utilized, that the experiments be carried out in a clean, vacant area with air aspiration (an empty fume hood), and that protective equipment be deployed by the researcher, **especially** eye protection (the latter I can personally certify!).

[I copied and pasted this warning notice from my earlier “Exploring” book, as it is just as applicable with these organic chemistry experiments as it is for the inorganic ones discussed earlier].

Another experimental concern is the possible reactivity of the sulfurane product with water, either in the liquid phase, or with water vapor in the atmosphere. Note that three other sulfur(IV) molecules, SO_2 , SOCl_2 , and SF_4 , all react very rapidly with water to form sulfurous acid (and HCl and HF in the latter two cases). Sulfuranes might conceivably hydrolyze to produce the corresponding **sulfoxide**:



A sulfurane (**sort of**) has actually been synthesized by the **reverse** of this hydrolysis reaction; that is, by the **dehydration** of a sulfoxide (ref. 11, page 47):

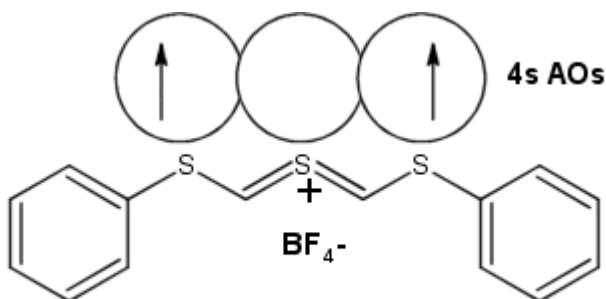


I say “sort of” a sulfurane, because the right-hand ring of the product is also aromatic, like the left-hand thiophene ring. The aromaticity in the two rings is probably a factor in the facile dehydration of the sulfoxide precursor to the sulfurane. The lesson we learn here is to ensure in the design of new molecular metal candidate molecules the inclusion of the sulfurane function

with one or two sulfur(II) thiol atoms , so as to obtain the metallic sulfur(III) [or NIOS valence] ; but the sulfurane function should **not** be part of an aromatic system , such as a thiophene ring . The “sixth” sulfur valence electron in an aromatic system sulfurane **won't** be promoted up into the 4s frontier orbital by the resonance ; instead , it will participate in the aromatic sextet of electrons .

As for the possible hydrolysis reaction of sulfuranes to sulfoxides , recall that PSN is subject to a slow reaction with either bulk water or water vapor in the air , its fresh surfaces tarnishing and turning gray as it “corrodes” like other reactive metals . The new metallic solids discussed in this report would probably behave chemically much like PSN , and sulfoxides might be possible reaction products .

One-electron oxidation of bis[(phenylthio)methylidene]sulfurane should activate the pi MO resonance , in the event that reproporationation to sulfur(III) doesn't occur spontaneously . The metallic solid should then crystallize from the reaction medium :

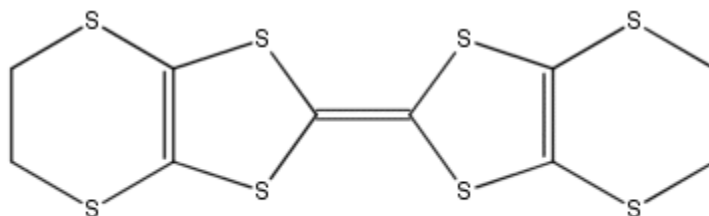


bis [(phenylthio)methylidene]sulfurane(1+) tetrafluoroborate

The molecule shown above is still in its **disproportionated** form , with localized pi bonds , because unfortunately my chemistry software apparently won't permit the drawing of dashed lines for resonating pi bonds . However , all three sulfur atoms in the molecule should be electronically equivalent , in effect in the sulfur(III) valence state , with their “sixth” valence electrons promoted up into the 4s frontier orbitals . I have arbitrarily removed the middle 4s electron in the sketch for a symmetrical artistic appearance .

This partially-oxidized sulfurane should be a Robin-Day Class IIIB mixed-valent compound and a molecular metal ; or , in my proposed general classification of metallic solids , it would be in Class 4 [the unoxidized parent sulfurane would also be a molecular metal if its sulfur(II) and (IV) spontaneously repropportionated to sulfur(III) ; in that case , it would be **homovalent** with respect to its electronically-active sulfur atoms , and not mixed-valent . However , it would be in Class 2 of the metallic solids] .

Both the unoxidized parent sulfurane and its partially oxidized offspring would be bronze metals , and certainly wouldn't be high temperature superconductors . The unoxidized sulfurane , even if it was metallic , probably wouldn't be a superconductor at any temperature , even very close to absolute zero . The partially oxidized derivative , though , could conceivably be superconducting , but only in the typical bronze metal range of 0 – 25 K (by "0" I mean close to absolute zero) . The current record for the highest transition temperature for any molecular metal superconductor is a derivative of the compound "ET" , bis(ethylenedithio)tetrathiofulvalene :

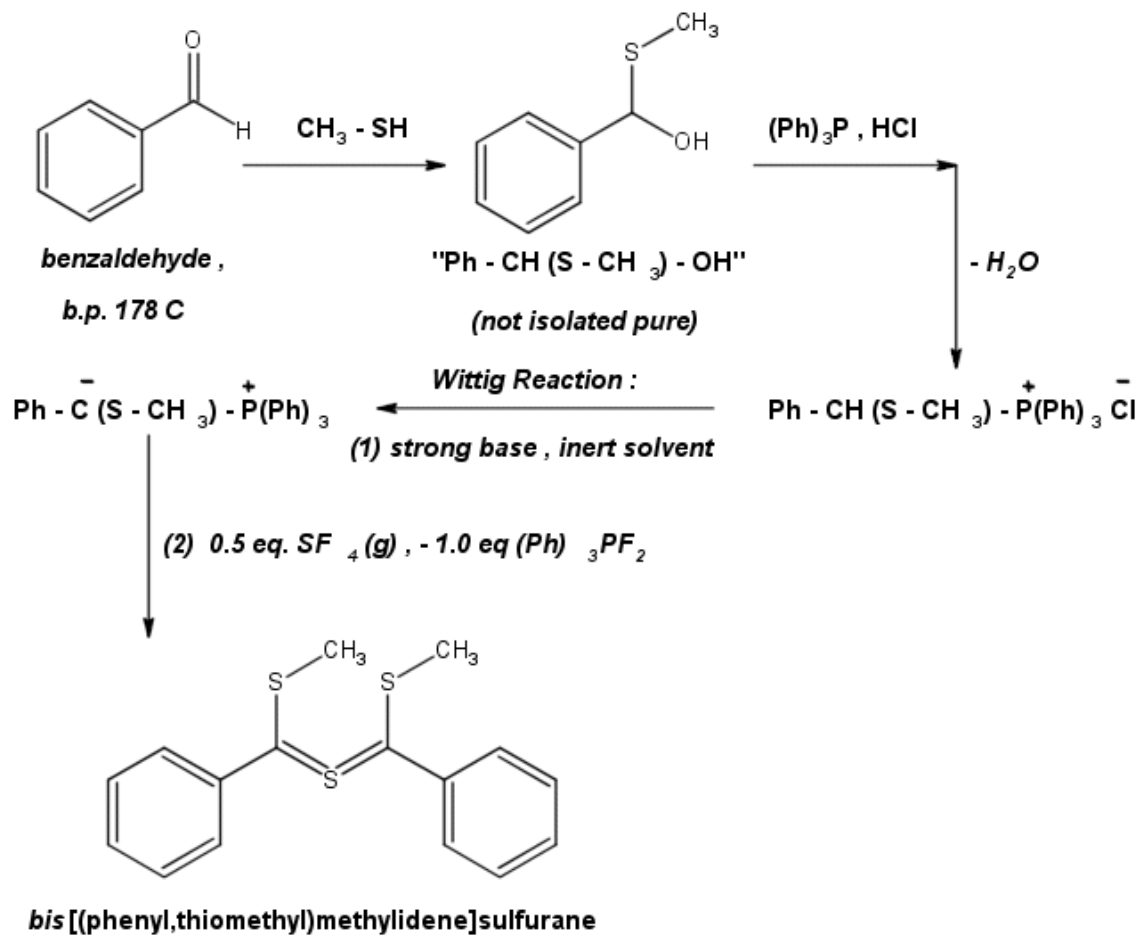


bis (ethylenedithio)tetrathiofulvalene , "ET"

Would the performance of the hypothetical new molecular metal compound bis[(phenylthio)methylidene]sulfurane(1+) tetrafluoroborate be able to surpass this still extremely frigid record of 12.8 K ? Note that the promotion mechanisms are different in the two molecules . In ET , it is **aromatization** of the two five-atom rings , to a thiophene-like configuration , that "kicks the sulfurs' sixth valence electrons upstairs" into the 4s frontier orbitals . In the sulfurane compounds it is the **reproportionation** of the sulfur(II) and (IV) valence states to sulfur(III) that forces the promotion of the "extra" sulfur electrons out of the skeleton . In the sulfurane , two or three electrons will be promoted in each molecule ; in the ET compound , possibly only one is ,

requiring the formation of **intermolecular** Cooper pairs in the superconducting state. However, as pointed out, we now would have the intriguing possibility of the formation of **intramolecular** Cooper pairs in the sulfuranes (still at a very low temperature, of course). But, as the coupling distances are generally shorter within the molecule than between two or more molecules, we might reasonably expect at least a slight increase in the transition temperature for the sulfuranes relative to those for the ET compounds.

As with the imidosulfurane discussed above, we can try to redesign the methyldene sulfurane molecule to “cluster” the three sulfur atoms closer together. Here are several ideas to consider, starting with scheme 4:

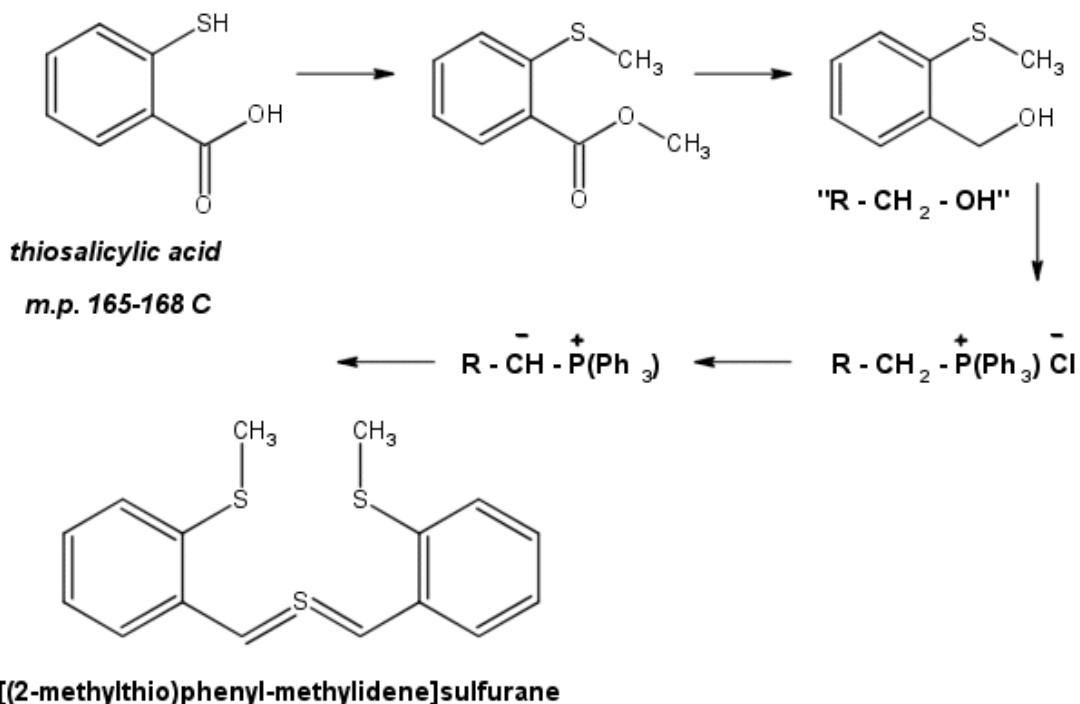


Note that alcohols are capable of alkylating triphenylphosphine in the presence of an acid (A. Maercker , p. 392 in ref. 8 , [page 47](#)) :



Benzaldehyde , triphenylphosphine , methylthiol , and HCl (concentrated aqueous acid and gas) might be combined together in a single one-pot reaction to provide the phosphonium salt , $\text{Ph-CH(S-CH}_3\text{)-P}^+(\text{Ph})_3 \text{Cl}^-$. This intermediate would then be used in the subsequent Wittig reaction , first being dehydrohalogenated to the zwitterionic ylid , $\text{Ph-C(S-CH}_3\text{)-P}^+(\text{Ph})_3$, then reacted with sulfur tetrafluoride to hopefully yield the sulfurane sketched above .

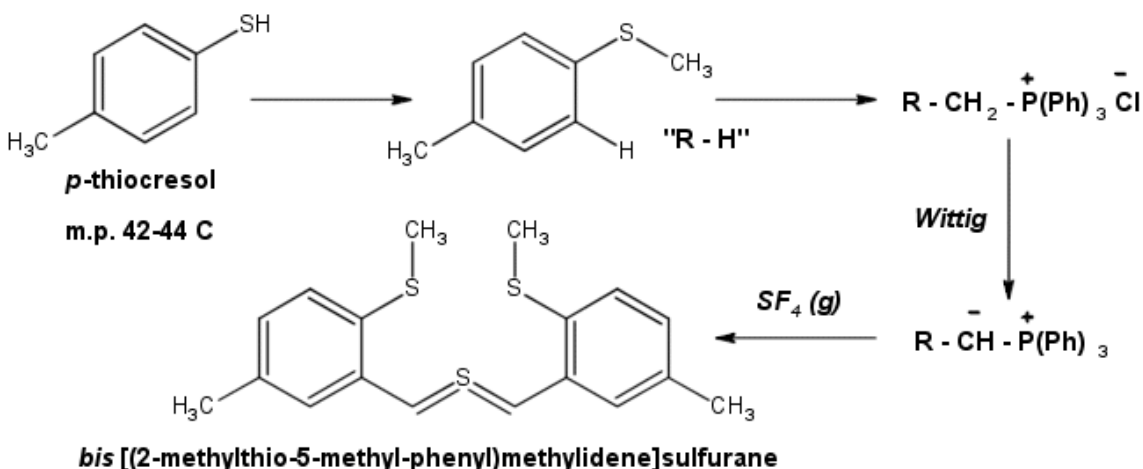
In scheme 5 , the methylenesulfurane target molecule resembles the imidosulfurane discussed earlier on [page 19](#) :



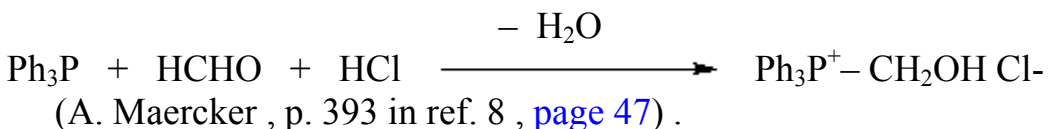
Exhaustive methylation of thiosalicylic acid (dimethyl sulfate, base) , followed by reduction of the ester function (LiAlH_4) should provide the

benzyl alcohol shown . Reaction of this intermediate with Ph_3P and HCl should yield the phosphonium chloride salt , which when treated with a strong base such as lithium hydride will generate the corresponding ylid betaine compound . Reaction of the ylid with SF_4 will hopefully give a good yield of the sulfurane .

In scheme 6 , the direct reaction of an activated benzene ring with formaldehyde and triphenylphosphine is suggested :



It might be possible in the alkylating step to use the reagent hydroxymethyltriphenylphosphonium chloride , prepared by the condensation of formaldehyde , triphenylphosphine , and HCl :

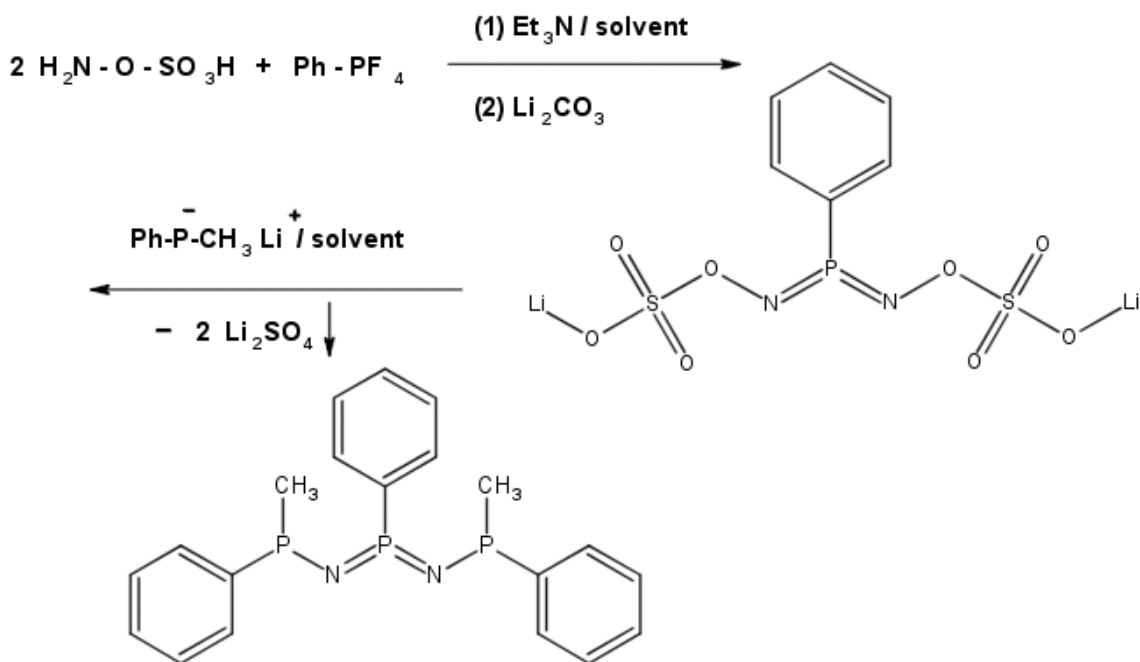


As a variation of this reaction , 4-chlorothiophenol (m.p. 49-51 °C , Aldrich Chemical) could be tried as starting material in place of the *p*-thiocresol . Doubtless the creative organic chemist could devise many more related compounds and analogues of the methylidene sulfuranes . The aim of these exercises in organic molecular design and synthesis should be to cluster the three sulfur atoms as closely together as possible , and in different geometrical arrangements if possible , trying to optimize T_c in the series .

A possible phosphorane molecular metal compound

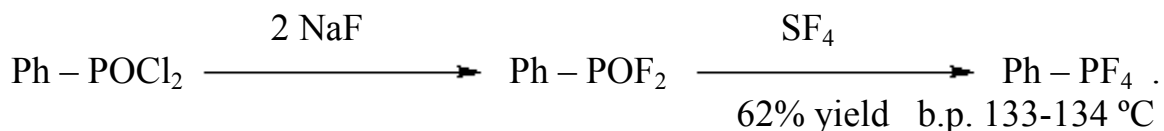
So far, sulfur(III) has been proposed as a source of metallic bond free electrons in novel molecular metal compounds. The repropportionated phosphorus(IV) valence, a “blend” of the conventional P(III) and P(V) valences, should also be examined as a potential electronically-active atom in new metallic materials.

The suggested chemical methodology used to produce phosphorus(IV) compounds is somewhat like that described earlier for the imido sulfuranes on [page 13](#), using the reagent hydroxylamine-O-sulfonic acid. A proposed synthesis of a phosphine-phosphorane molecular metal candidate compound is outlined below in scheme 7:



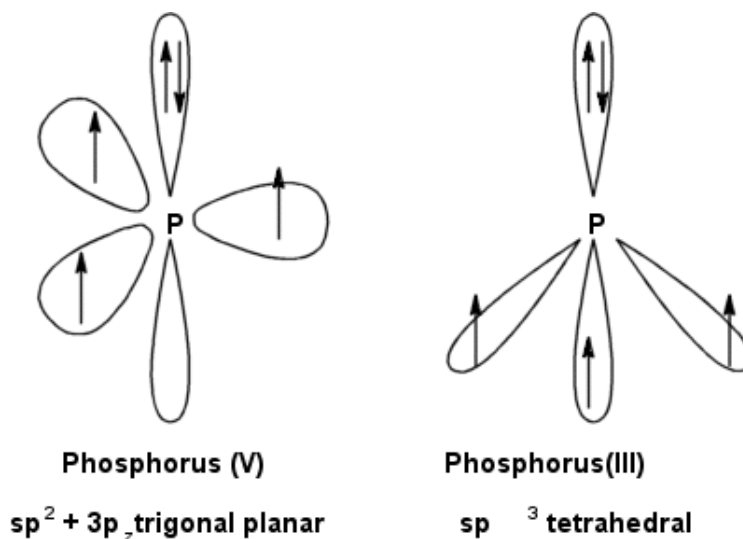
bis [N-(methylphenylphosphine)imido]phenylphosphorane

The intermediate phosphorus(V) compound, phenyltetrafluorophosphorane, would take the place of sulfur tetrafluoride with the hydroxylamine-O-sulfonic acid. Ph-PF₄ has been prepared by Smith (ref. 9, page 47) from the commercially available phenylphosphonyl chloride (Aldrich Chemical) :



Methylphenylphosphine is commercially available (Aldrich Chemical), but it is very expensive, toxic, and pyrophoric: three rather undesirable characteristics! A strong base, such as n-butyl lithium, would be required to deprotonate the phosphine to the anion, as has been done with diphenylphosphine (ref. 12, page 47), which also might be tried in these experiments.

As with the sulfur analogues, the imido phosphorane might require one-electron oxidation to induce reportionation of the P(III) and P(V) atoms in the molecule to the metallic P(IV). In the disproportionated form (shown in the sketch above) the phosphine atoms should be tetrahedral, while the phosphorane atoms would be trigonal planar in configuration :



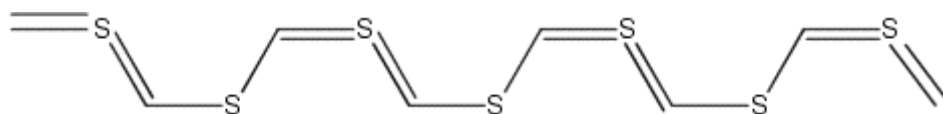
In the repropportionated form , with resonance through the pi MOs , all three phosphorus atoms in the molecule are trigonal planar (+ $3p_z$ native AO) as shown for phosphorus(V) in the sketch above . The “fifth” valence electrons would be promoted into the 4s frontier orbitals , by analogy with the isoelectronic sulfur atoms in the sulfuranes (the “fourth” valence electrons would be in the $3p_z$ AOs , forming an extended pi MO with the nitrogens’ $2p_z$ AOs) .

On a practical note , these imido phosphoranes should be thermally quite stable , in contrast to the relatively unstable S–N compounds discussed earlier . The precursor phosphorus(III) compounds , the phosphines , are extremely reactive , and indeed are pyrophoric [reacting spontaneously with atmospheric oxygen] , requiring an inert atmosphere of nitrogen or argon for their safe manipulation . However , once bonded with nitrogen as a **phosphoramidate** compound , they become fairly unreactive ; cf. the high boiling solvents hexamethylphosphorus triamide , $[(CH_3)_2N]_3P$, and hexamethylphosphoramidate . There is also the example of the **phosphonitrilic chlorides** , a family of synthetic inorganic elastomers noted for their thermal and chemical resistance : $-[N = P(Cl)_2]_n-$. However , even though the component imido phosphorane molecules are expected to be chemically stable , their repropportionated form in the metallic solid should still be easily oxidized by atmospheric oxygen and moisture , as a 4s sigma XO metallic bond would be , although not as rapidly as , say , the corresponding isoelectronic alkali metal , potassium (**very quickly !**) .

Poly(methyldiene) sulfurane

Consideration of the methyldiene sulfurane molecular metal candidate compounds ([page 20](#)) , whose structures were originally inspired by that of poly(sulfur nitride) , brings us full circle back to macromolecular metals . Could we devise a new polymeric metallic solid whose structure utilizes sulfur(III) as the source of its metallic bond free electrons ? MacDiarmid et al. had pointed out the theoretical possibility of substituting CH and CR for the inert nitrogen linkages in PSN (p. 71 in ref. 1 , [page 46](#)) .

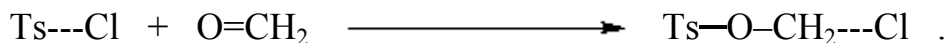
The polymer would then have the empirical formula $(\text{HCS})_x$, and the structural formula ,



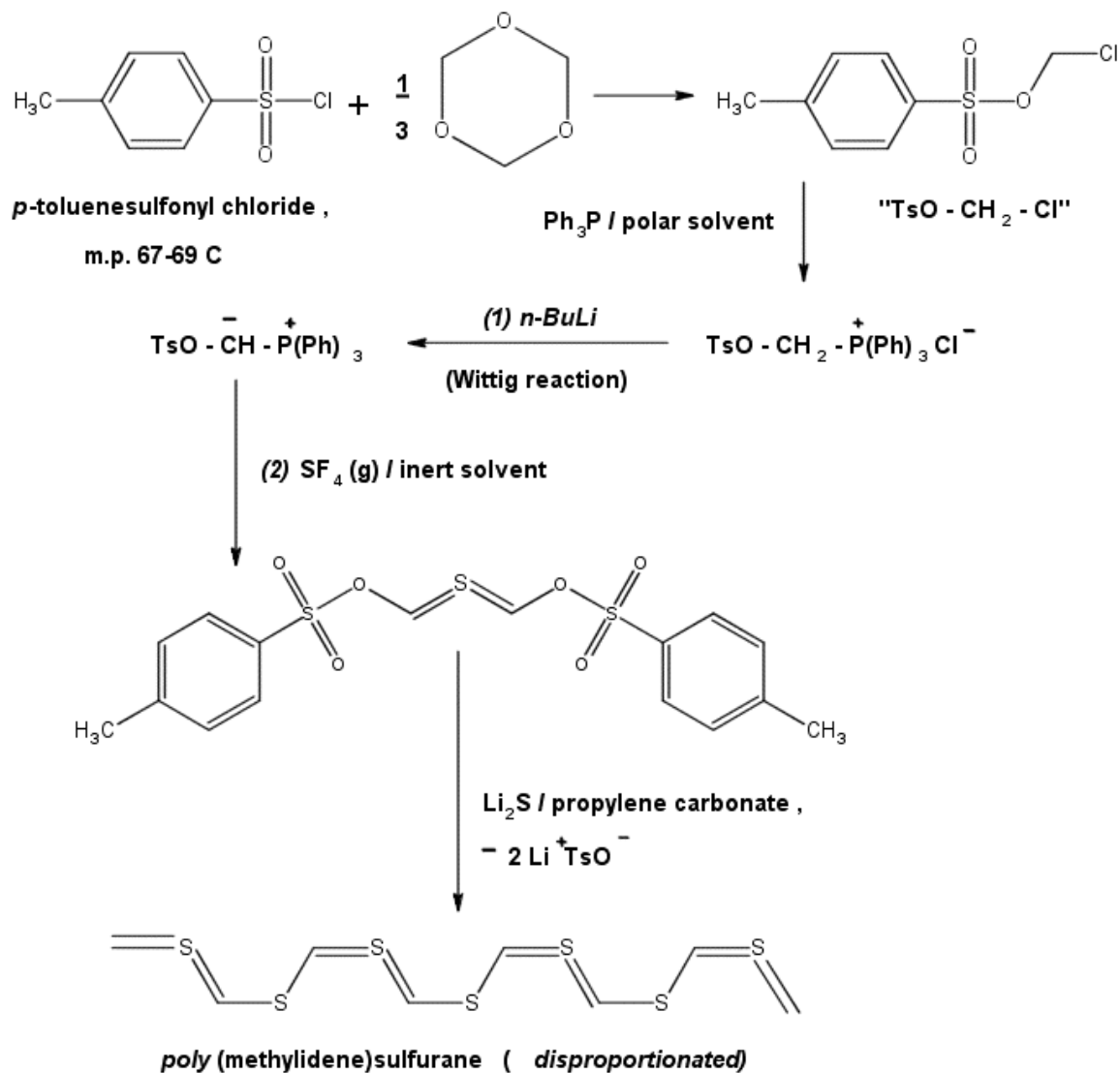
(This is the **disproportionated** form ; I can't seem to draw the **reproportionated** form of it properly with my limiting chemistry software) .

Again , we note the alternating sulfur(II) and sulfur (IV) functionalities ; reproportionation of the thiol and sulfuranes to sulfur(III) should make the polymer metallic in nature , with promotion of the “sixth” sulfur valence electrons up into the frontier 4s orbitals , as is thought to happen in PSN . This reproportionation may or may not be spontaneous when the polymer is synthesized ; it may have to be induced by a partial one-electron oxidation of the thiol sulfur atoms by , say , nitrosonium tetrafluoroborate , NO^+BF_4^- .

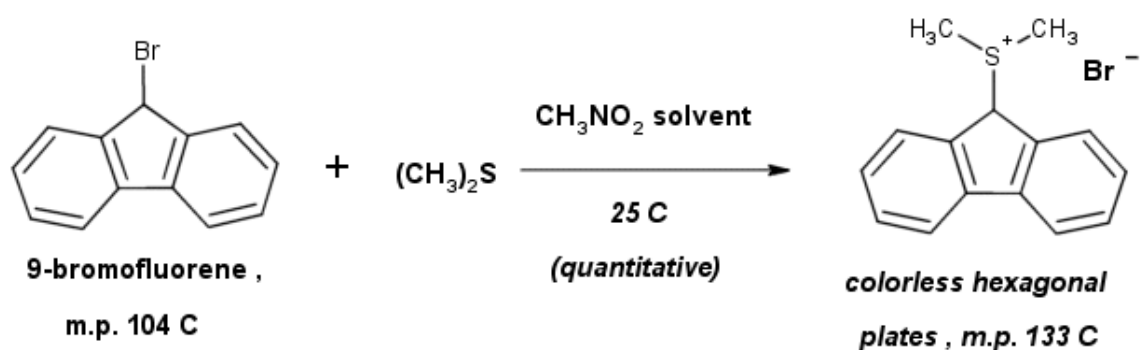
Two possible synthesis routes to poly(methylidene)sulfurane come to mind . The first is related to that one outlined in scheme 1 on [page 13](#) , and its modification for a possible preparation of PSN , as shown on [page 14](#) . Scheme 8 is presented on the following page . The first reaction in the sequence is that of p-toluenesulfonyl chloride (“tosyl chloride”), a familiar organic chemistry reagent , with 1,3,5-trioxane , a solid trimer of formaldehyde . This combination takes advantage of a lesser-known organic reaction , the addition of acyl halides to the carbonyl group of aldehydes (ref. 13 , [page 47](#)) . In our case , the S–Cl bond in tosyl chloride is labile , while the S–O bond in the product is very strong :



The second step involves the preparation of the quaternary phosphonium chloride salt from the combination of equimolar quantities of the chloromethyl tosylate ester product above with triphenylphosphine . This addition might be facilitated by the use of a **polar** organic solvent for the two reagents . There is an interesting precedent for the use of such a solvent .



Ingold and Jessop noted that 9-bromofluorene and dimethylsulfide failed to react either neat or in low polarity solvents such as benzene and ether . However , in a highly polar solvent like nitromethane , the reaction (at room temperature) was both immediate and quantitative (ref. 14 , [page 47](#) ; sketch on the next page) . This is a useful “trick” that chemists might keep in mind for the preparation of quaternary ammonium , sulfonium , and phosphonium halide salts . In particular , the Wittig reaction utilizes such quaternary phosphonium halide salts as the intermediates leading to the ylid betaines , the actual Wittig reagents , so this discovery made over seventy years ago

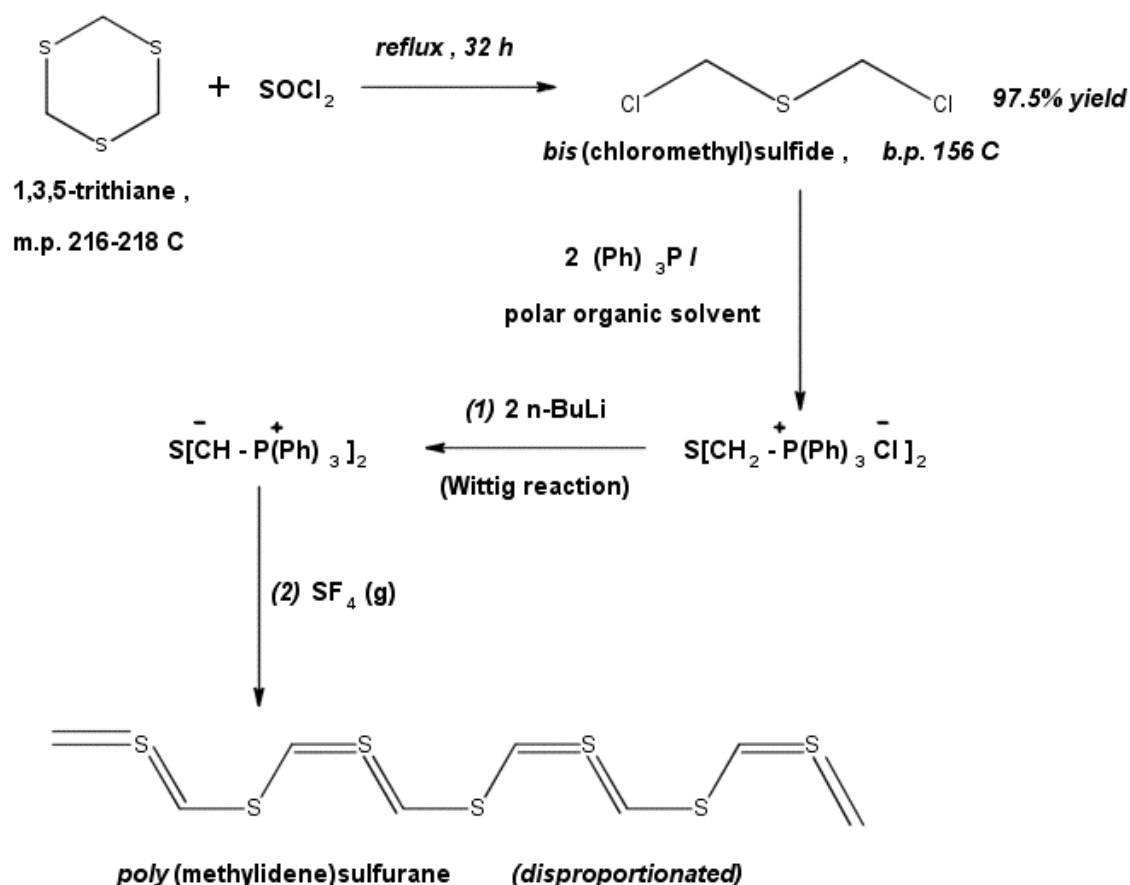


will be very helpful to us in this modern era as we work with the Wittig reaction .

The quaternary phosphonium chloride salt is then transformed in the Wittig reaction , first by dehydrohalogenation with a powerful base such as n-butyl lithium (see the review of the Wittig reaction by A. Maercker , ref. 8 , [page 47](#) , for a survey of such bases and experimental descriptions) , then by condensation of the ylid with sulfur tetrafluoride , to produce the key intermediate , bis(methylidene-1,3-tosylate)sulfurane . In the final step of scheme 8 , this latter difunctional reagent is combined with sulfide anion , which provides the sulfur(II) “thio” atoms in the polymer . Lithium sulfide (commercially available , eg. Alfa Aesar) is suggested as the sulfide source , as lithium salts are generally more soluble in organic solvents than are those of the other alkali metals .

The highly polar solvent , propylene carbonate (PC) , b.p. 240 °C , which can dissolve appreciable quantities of inorganic salts (ref. 6 , [page 46](#)) , is proposed for trial in this polymerization reaction . Because this is a type of **condensation polymerization** , with increasing concentrations of inert by-product accumulating in the reaction vessel and retarding the reaction progress , we cannot reasonably expect a very high molecular weight for the poly(methylidene sulfurane) product . There is also no guarantee it will be repropportionated to the “all-sulfur(III)” metallic solid , either , but I suspect that like PSN , it probably will spontaneously become metallic as it is formed in the reaction mix . This may result in the gradual precipitation from the solution of a fine-grained , insoluble , crystalline product as a low molecular weight form of the desired poly(methylidene)sulfurane .

The second approach to this metallic polymer again uses SF_4 as the sulfur(IV) sulfurane source, but this time the relatively obscure organic compound bis(chloromethyl sulfide), $(\text{ClCH}_2)_2\text{S}$, is proposed as the sulfur(II) “thio” atoms source. The synthesis is outlined in scheme 9:



Assuming there isn't a commercial source of the starting material, bis(chloromethyl) sulfide, at a reasonable cost (it apparently isn't offered by Aldrich Chemical Co., a prominent supplier of fine organic reagents), the researcher would have to prepare a quantity of it using a procedure published in the chemical literature. Fortunately, there are several good preparations of α -halosulfides generally, and of bis(chloromethyl) sulfide specifically (ref. 15, page 48). The one I outlined above in the first step was published by Truce, Birum, and McBee, and seems to be the simplest one for small-scale laboratory practice (the aqueous reaction with formaldehyde,

HCl , and H₂S [gas , or NaSH precursor] , patented by the German chemical company Hoechst in 1960 , is probably the most economical synthesis of the sulfide , but more suited for pilot plant or production-scale application) .

I should advise the interested reader that bis(chloromethyl) sulfide **apparently** seems to be relatively innocuous physiologically , at least in comparison to its rather ghastly cousin , bis(2-chloroethyl) sulfide , the infamous “mustard gas” of World War I notoriety . The German chemists , Bloch and Höhn , who first prepared bis(chloromethyl) sulfide around 1922 , described it as “..... a faintly yellowish oil of peculiar ethereal chloroform-like odour” (it must have taken considerable courage to sniff cautiously their reaction product !) .

This is somewhat reassuring , but as with all chemistry experimentation , suitable precautions must be taken to avoid injury or harm . First and foremost , of course , is the prime directive to avoid any and all unnecessary contact with the chemicals one is working with . Even before that , though , the researcher should carry out a thorough literature study , not only to become acquainted with the “prior art” , but also to learn as much as possible about the materials being handled in his or her project , so as to be able to fully implement safety precautions **before** embarking on the actual laboratory work .

For example , it is now well known that in any reaction involving aqueous formaldehyde and HCl , the highly obnoxious bis(chloromethyl) ether , (ClCH₂)O , is inevitably produced . This compound is known to be a very active **carcinogen** (ref. 16 , [page 48](#)) . Therefore , researchers are recommended to avoid an aqueous route to bis(chloromethyl) sulfide , eg. the Hoechst preparation . The trithiane-thionyl chloride route outlined above employs non-aqueous conditions , and so is probably a safer procedure for the preparation of bis(chloromethyl) sulfide . Nevertheless , any interested researcher should exercise all due caution when preparing and handling the chemical compounds discussed in this report ([and generally , elsewhere ; please see my note about this on page 22](#)) .

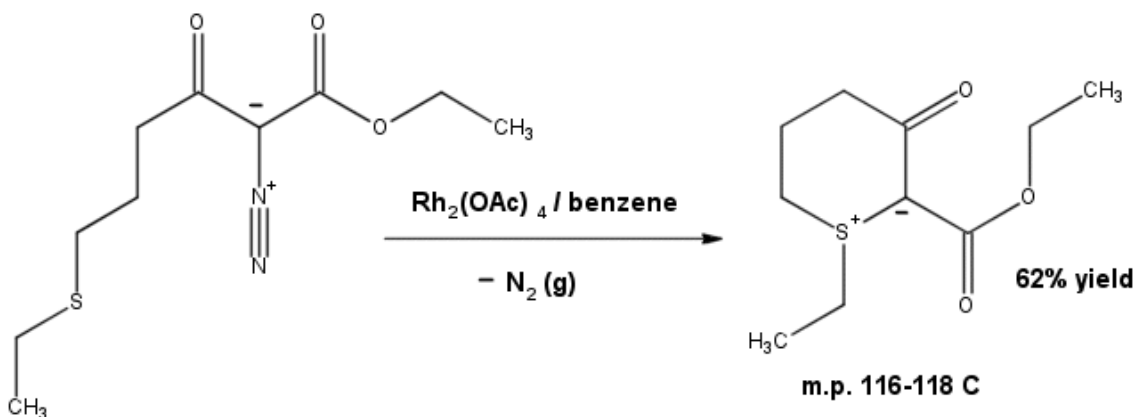
The second step of the polymer synthesis involves the quaternization of the

sulfide with **two** equivalents of triphenylphosphine . As mentioned above on [page 33](#) , a polar solvent undoubtedly would assist this salt formation . A suitable polar solvent might be nitromethane , acetonitrile , or even the mundane acetone (methanol , ethanol , or isopropanol might be acceptable also , but they could conceivably react with the sulfide) .

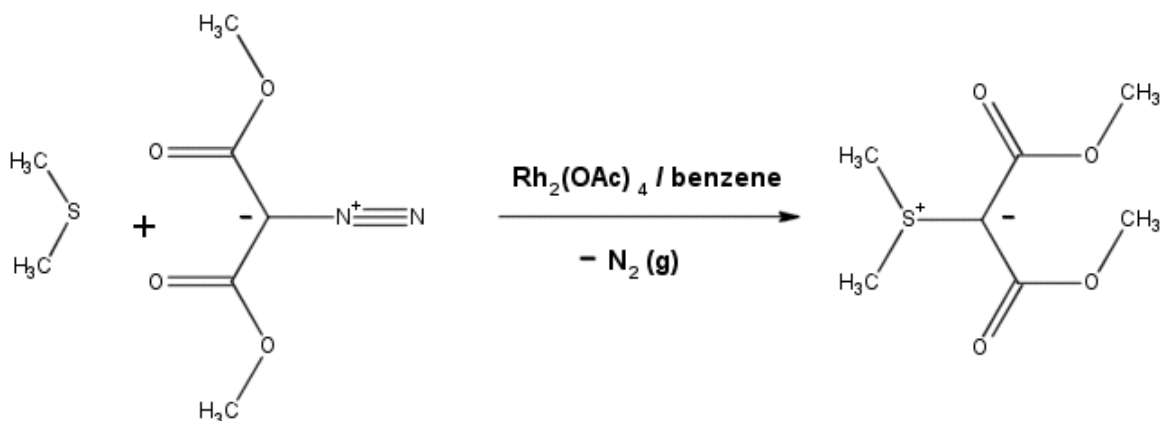
The third step is the preparation of the Wittig ylid , $[(\text{Ph})_3\text{P}^+ - \text{CH}^-]_2\text{S}$, and its polymeric condensation with SF_4 . Will the ylid , with all those ionic charges , be stable enough to generate and use in the reaction ? At this stage of the preparation it is difficult to predict with certainty the outcome of events in this unique , novel system . That's where experiment alone should yield the answers that theory can't provide .

Poly(S-methyl-methylidene)sulfurane

Diazomethane and its derivatives are known to react with sulfides (thioethers) to produce sulfonium carbanion betaine (ylid) adducts . Two examples from the research literature will illustrate this interesting reaction :

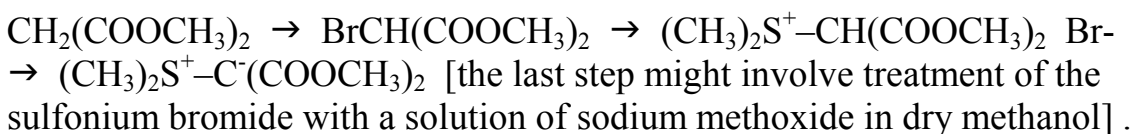


(Moody and Taylor , ref. 17 , [page 48](#)) .



(Ando, ref. 18, [page 49](#)).

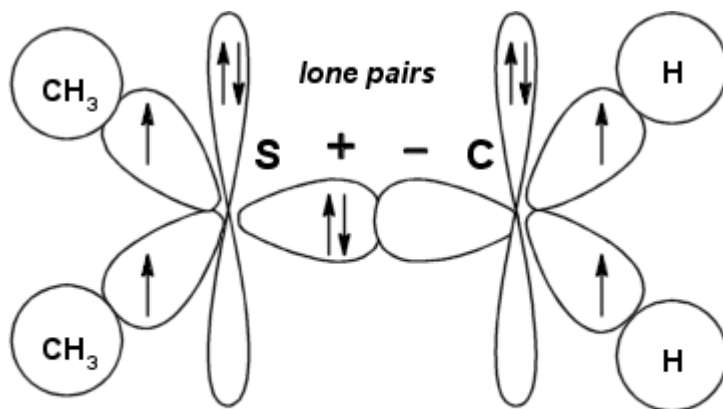
Note that the carbanion in each example is strongly stabilized by electron resonance over the neighboring carbonyl groups; in the first case, the anion is in a β -ketoester system (like acetoacetate); in the second, it is in a malonate ester. To put the matter in a more familiar perspective, the latter malonate molecule could probably be synthesized by a conventional route such as:



Rhodium acetate dimer seems to be the specific catalyst for this reaction, which is usually carried out in refluxing benzene (b.p. 80 °C). Its main thermodynamic driving force is the expulsion of the extremely stable nitrogen molecule.

Alkylidene sulfurane compounds, with simple alkyl substituents, are also known. For example, the molecule $(\text{CH}_3)_2\text{S} \rightarrow \text{CH}_2$ can be handled at around -10°C ; the compound $(\text{CH}_3)_2\text{S} \rightarrow \text{C}(\text{CH}_3)_2$ is less stable, being prepared and manipulated only at about -70°C (ref. 19, [page 49](#)). The trend in stability of these alkyl-substituted sulfuranes follows the trend in stability of **carbanions**: primary > secondary > tertiary. The suggestion is therefore that they have a significant carbanion character; eg. $(\text{CH}_3)_2\text{S}^+ - \text{CH}_2^-$.

Is it correct to write the formula of the last compound $(\text{CH}_3)_2\text{S}=\text{CH}_2$? We have , after all , the well known sulfur(IV) compound thionyl chloride , whose formula is often written as $\text{Cl}_2\text{S}=\text{O}$. The sulfur and carbon atoms in the sulfurane could have a **trigonal planar ($\text{sp}^2 + \text{p}_z$)** structure :



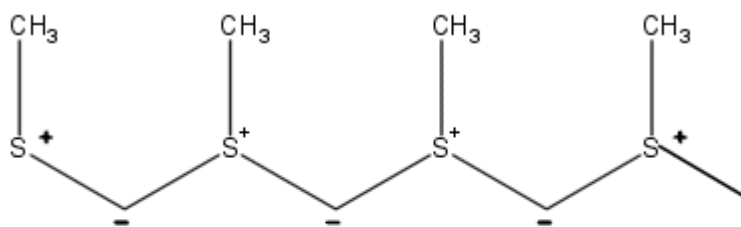
(S,S-dimethyl-methyldene)sulfurane , betaine form

We see from this simple sketch that we cannot draw an “olefinic” structure for the sulfurane , and that the “betaine form” , with the electronegative carbon atom , actually seems to be a fairly accurate description . We could equally well write a structure for the sulfurane molecule in which both the sulfur and carbon atoms have a **tetrahedral (sp^3)** structure (**I don't know if the molecular structure , i.e. geometrical shape , of the sulfurane molecule has been determined yet**) . In both cases , we see that the sulfur atom is donating one of its electron pairs to the carbon ; it thus becomes positively charged , and the carbon becomes negatively charged (that is , the sulfur-carbon bond in the compound is **coordinate covalent , or dative , \rightarrow**) .

As for thionyl chloride , its sulfur atom is probably tetrahedral in structure , with the chlorine atoms replacing the methyl groups in the sketch above , and an oxygen atom (with its six valence electrons) receiving the dative electron pair from sulfur ; a lone pair of electrons occupies the fourth sigma lobe on the sulfur atom . So the formula for thionyl chloride could perhaps more realistically be written as $\text{Cl}_2\text{S}\rightarrow\text{O}$ (**I don't know what its geometry is , either**) .

The idea for synthesizing a new polymeric metal utilizing the reaction of a diazomethane compound with a sulfide (thioether), was to design a molecule in which the diazo part ($-\text{N}_2^+$) was at one end of the molecule, and the sulfur(II) “thio” atom was at the other: $\text{CH}_3 - \text{S} - \text{C}^-\text{H} - \text{N}_2^+$; that is, **methylthiodiazomethane**. When treated with rhodium acetate dimer in benzene, a **carbene** intermediate is thought to form when the nitrogen molecule is ejected from the diazomethane precursor. In our case, that would be: $\text{CH}_3 - \text{S} - \text{C}^-\text{H} - \text{N}_2^+ \rightarrow \text{CH}_3 - \text{S} - \text{CH} : + \text{N}_2(\text{g})$. The electrophilic carbene carbon bonds to the nucleophilic sulfur atom with the $\text{S} \rightarrow \text{C}$ dative bond, as shown in the sketch on the preceding page. Since the methylthiodiazomethane molecule is bifunctional, it should be able to polymerize, forming an **addition polymer** (as with polyethylene, polypropylene, polystyrene, etc.; there are no by-products, as in the condensation polymers discussed earlier, hence we may be able to have a relatively high molecular weight polymer).

The polymer could have a “betaine form”:

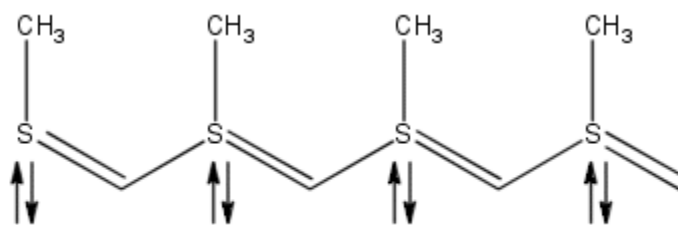


poly (S-methyl-methylidene)sulfurane

(betaine form)

Look at all those charges on the chain! Is that realistic? Let's suppose the sulfur and carbon atoms in the chain could instead form a genuine polyolefinic bond along it, as in repropportionated $(\text{SN})_x$ [sketch, [page 8](#), lower structure]. That is, both the sulfur and carbon atoms have the “standard” trigonal planar $\text{sp}^2 + \text{p}_z$ structure. This is fine for the carbons, but the sulfurs have room for only four of their six valence electrons in this bonding arrangement. As with PSN and the other molecular and polymeric metals proposed earlier, the two “extra” sulfur electrons will have to be promoted

up into the 4s frontier orbital , above the covalent chain skeleton . Sulfur can undoubtedly promote **one** extra electron into the 4s orbital , but can it really promote **two** electrons ? In order for the polymer to have metallic properties there would have to be some leakage of some of the 4s electron density into the 4p orbitals ; that is , the polymer would have to be isoelectronic with the alkaline earth metal **calcium** . The “metallic structure” of the polymer could now be written as :

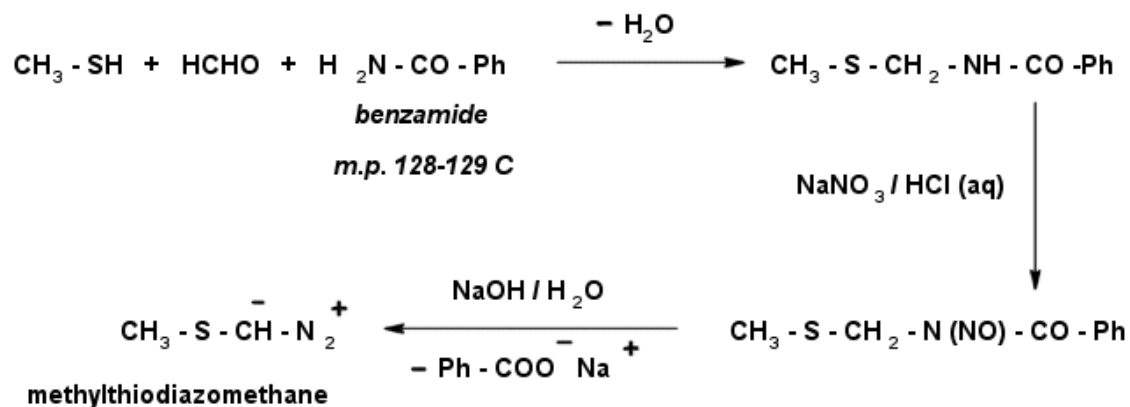


poly (S-methyl-methyldene)sulfurane (metallic form)

In this form , the polymer is stabilized by the **three** bonds : the low energy sigmas , the medium energy pi bonds , and the higher energy sigma-pi XO metallic bond . Plus , there are no ionic charges (or even partial charges) anywhere in the chains . It seems to me that this would be a much stabler , stronger structure than the “betaine form” sketched above , even if sulfur does have to promote two valence electrons from the 3 s-p to 4 s-p levels .

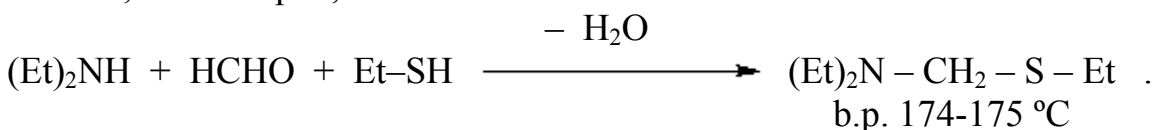
That is the central supposition on which the concept of this particular polymeric metal is based . As always , there is only one sure way to confirm or refute this hypothesis : by experiment . We will have to devise a synthesis of the key intermediate, methylthiodiazomethane , then subject the compound to catalytic decomposition – and we hope , a successful polymerization – in the presence of rhodium acetate dimer in benzene .

A proposed synthetic route to methylthiodiazomethane is outlined in scheme 10, presented at the top of the following page . The first step is related somewhat to the Mannich reaction , and relies on the fact that primary amides are generally capable of forming N-methylol amides with formaldehyde : $\text{Ph} - \text{CO} - \text{NH}_2 + \text{CH}_2=\text{O} \rightarrow \text{Ph} - \text{CO} - \text{NH} - \text{CH}_2\text{OH} .$



(Zaugg and Martin , ref. 20 , [page 49](#)) .

A similar sort of reaction has been carried out with amines in place of amides ; for example ,



(McLeod and Robinson , ref. 21 , [page 49](#)) .

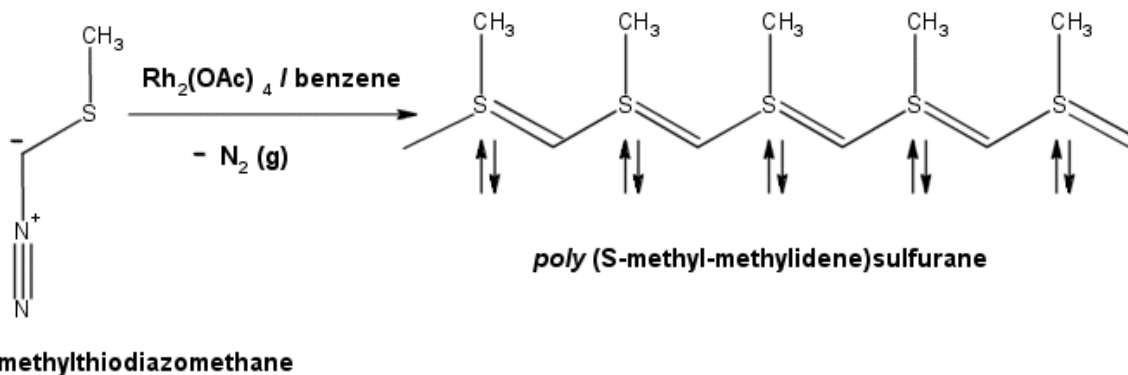
I have suggested the use of the relatively high melting , common amide benzamide as a starting material , so that the two subsequent intermediates should be crystalline solids with moderate melting points . This would make them much easier to purify (by crystallization from suitable solvents) , than if they were oils requiring fractional distillation under a high vacuum .

The second step involves nitrosation of the now-secondary amide . There are several methods to accomplish this ; I have indicated the commonest and simplest procedure , with a nitrite salt and mineral acid . Various nitrosating systems and laboratory techniques , both aqueous and non-aqueous , are discussed in the textbook literature (ref. 22 , [page 49](#)) .

The third step is the actual preparation of the target molecule , methylthiodiazomethane . It should be possible to accomplish this by treatment of the N-nitrosoamide with aqueous base , such as NaOH .

There is a detailed review of diazomethane , including methods for preparing it , in Organic Reactions (ref. 23 , [page 50](#)) . The interested reader should consult this reference for important information on the safe preparation , handling , and use of the highly toxic and potentially hazardous diazomethane . Methylthiodiazomethane might very well marry together the worst characteristics of the two component parts of the molecule : the methylthio part , which might have an awful stench like dimethyl sulfide ; and the diazomethane part , which is unstable and potentially explosive . Diazomethane is an active alkylating agent , and such chemicals are often potent **carcinogens** [cf. bis(chloromethyl) ether , dimethyl sulfate , β -propiolactone] , so again the prospective researcher should be well aware of the potential hazards involved in the handling of such chemicals .

Assuming the target molecule can actually be synthesized and characterized in a reasonably pure state , and in sufficient quantity , the final step in the proposed route to the metallic polymer would be the polymerization :



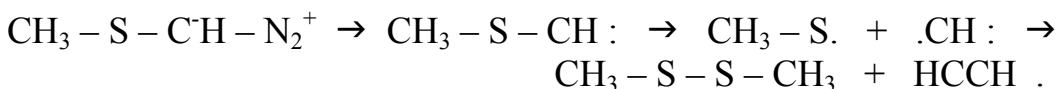
As mentioned earlier , rhodium acetate dimer seems to be the catalyst of choice for the diazomethane decomposition to the corresponding carbene (UV light can also be used for this) . Benzene , under reflux (80 °C) , is the usual solvent . I wonder if the $\text{Rh}_2(\text{OAc})_4$ is benzene-soluble . If not , would a **polar** solvent , such as acetonitrile (b.p. 82 °C) , dissolve the catalyst and be more effective ? Another technique is to dissolve the catalyst in a volatile solvent such as acetone , then spread this solution evenly over the inside of the polymerization vessel , letting the solvent evaporate and coating a thin layer of the catalyst on the interior of the flask . A solution of the monomer

in a solvent that doesn't dissolve the catalyst is then placed in the flask . Polymerization occurs at the surface of the catalyst , leaving a film of polymer over the inside of the flask wall . This sort of technique was used in the preparation of thin films of the interesting material polyacetylene , polymerizing acetylene gas in the presence of a Ziegler-Natta type of catalyst . Polyacetylene itself is essentially an insulator , even though it has a shiny , metallic appearance somewhat like stainless steel ; partial one-electron oxidation of $(\text{CH})_x$, for example by iodine , will convert it into an electrical conductor and metallic solid with a golden color and luster (ref. 24 , page 50) .

Rhodium acetate dimer is one of a family of transition metal acetate dimers with characteristic crystal structures . I discussed them briefly in the "Exploring" book (page 80 ; see especially Figure 14 , the structure of $\text{Cu}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$) . Would it be possible to catalyze the decomposition of the diazosulfide with another dimeric acetate , such as that of anhydrous copper(II) acetate , or cobalt(II) acetate , or molybdenum(II) acetate ? Possibly other transition metal complexes with known catalytic activity could be tried in this final critical reaction . One that comes to mind is "Wilkinson's catalyst" , tris(triphenylphosphine)rhodium(I) chloride , $(\text{Ph}_3\text{P})_3\text{RhCl}$. This square planar coordinate covalent compound is soluble in many organic solvents – benzene , too – and is most often used as the soluble catalyst in **homogeneous hydrogenation** . It accomplishes this when the hydrogen atoms displace the labile chlorides from the square plane of the complex . Could the reactive carbene intermediate be similarly stabilized in Wilkinson's catalyst before polymerization ? Would the isoelectronic complex $(\text{Ph}_3\text{P})_3\text{CoCl}$ perform similarly with the diazosulfide ? Both complexes are commercially available , eg. from Aldrich Chemical , Alfa-Aesar , Strem Chemicals , etc. (the latter firm offers a wide array of transition metal catalysts for a multitude of chemical transformations) .

I mention all of these possibilities , because catalysis is often more of an art than a science . It would be a shame to go to a lot of trouble and expense to prepare what is surely a vile substance , only to find that the much-touted catalyst to decompose it to the carbene fails to accomplish the desired task .

It may be energetically rather forbidding to polymerize the carbene to a metallic polymer, and the reaction course could veer away from that path. Instead, the researcher may end up with insoluble, non-metallic “gunk” in the polymerization flask. For example, the carbene may form, but then dissociate into free radicals:



The latter products are dimethyl disulfide and acetylene, both well-known compounds. Or, the methylidene part might polymerize into a waxy solid like polyethylene. Thus, choosing or discovering the right catalyst to stabilize the carbene and permit it to smoothly polymerize to the metallic polymer may well be of critical importance to the success of the polymer preparation. The researcher will also have to decide, or experiment, on whether to use a soluble catalyst to effect **bulk polymerization** of the carbene monomer (probably producing a grainy precipitate of polymer), or using the insoluble “film” technique mentioned above to effect a **surface polymerization**, resulting in a thin coating of metallic polymer on the reaction flask inner wall, as with polyacetylene.

As noted earlier, UV (ultraviolet) light also causes the diazo compounds to decompose into carbenes and nitrogen. A simple technique like irradiating a solution of methylthiodiazomethane in a suitable solvent, contained in a quartz flask, may be sufficient to deposit a shiny metallic film of poly(S-methyl-methylidene)sulfurane on the inner surface of the flask. In any case, whatever the approach taken to synthesize the polymer, it presents new possibilities for expanding our understanding of metallic solids, and should be an exciting challenge to the creativity and ingenuity of chemists.

While efforts to synthesize all (or some) of these proposed new molecular and polymeric metals may or may not be successful, I nevertheless hope that this discussion will arouse the interest of researchers in them, and in the study of metallic solids in general. Most importantly, along the way a lot of fascinating new chemistry will have been explored and developed.

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