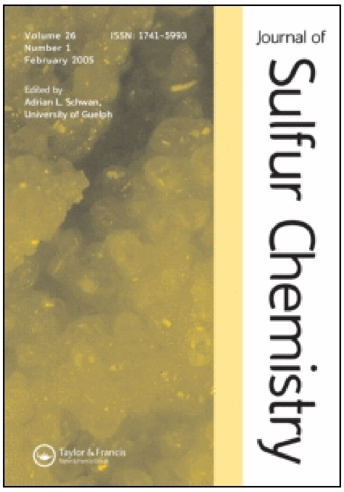

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NEW REACTIONS AND CHEMICALS BASED ON SULFUR AND ACETYLENE[†]

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A new branch of organic sulfur chemistry based on acetylene, developed only recently, has produced novel reactions and chemicals of interest for both fine synthesis and large-scale industry.

Reactions of sulfur and chalcogen nucleophiles with acetylenes in superbasic media and some prospective applications of these reactions are discussed. Some synthetic uses of the now technically available compounds divinyl sulfide and divinyl sulfoxide are also described.

CONTENTS

[†] The paper is based on a plenary lecture held at the Tenth International Symposium on the Organic Chemistry of Sulfur (Bangor, Wales, September 5–10, 1982).

I. INTRODUCTION

With the shortage of oil and natural gas on a worldwide scale, acetylene, which can be independently made from coal, is now returning to its lost position as the preeminent source of chemicals.[1–3]

Sulfur is known to be a very cheap element, available industrially with unusual simplicity and in enormous quantities.[4] Thus both sulfur and acetylene have a real chance to become basic raw materials in a changing economic and technological environment. Therefore, the sulfur-acetylene marriage is a requirement of the time. It is believed that sulfur should occupy one of the key positions in the renaissance of the acetylene-based industry.

The following types of sulfur-acetylene reactions may have a multi-tonnage future: insertion of acetylene into the H—S (1), S—S (2), and halogen—S (4) bonds, addition of thione compounds to the triple bond (3) and cleavage of the S—S bond with the acetylide carbanion (5).

1. $\mathrm{H{-}S + HC{\equiv}CH \longrightarrow H_2C{=}CH{-}S}$
2. $\mathrm{S{-}S + HC{\equiv}CH \longrightarrow S{-}CH{=}CH{-}S}$
3. $\mathrm{S{=}C + HC{\equiv}CH \longrightarrow \overset{\ominus}{HC}{=}CH{-}S{-}\overset{\oplus}{C}}$
4. $\mathrm{Cl{-}S + HC{\equiv}CH \longrightarrow ClHC{=}CH{-}S}$
5. $\mathrm{1/8\ S_8 + HC{\equiv}C^{\ominus} \longrightarrow HC{\equiv}C{-}S^{\ominus}}$

This paper covers nucleophilic reactions, mainly of the first three types.

II. ACTIVATION OF ANIONS AND TRIPLE BONDS WITH SUPERBASIC SYSTEMS

About a decade ago, unexpectedly wide synthetic possibilities were opened with the introduction of superbasic systems into acetylene chemistry and especially into its sulfur part.[5,6] These systems greatly facilitate the known nucleophilic additions to the triple bond and allow new reactions which seemed impossible previously. The term "superbasic system" covers systems which consist of a strong base (alkali metal hydroxides, alkoxides, or amides) and an aprotic ligand (sulfoxides, phosphoryl triamides, phosphine oxides, ammonia, crown ethers, cryptands, and the like) capable to bind the alkali metal cation and by this way separating the contact ion pair of the base, making its anion poorly solvated ("naked").

$$\underset{\text{contact ion pair}}{\mathrm{M^{\oplus}B^{\ominus}}} + \mathrm{n\cdot L} \rightarrow \underset{\text{separated ion pair}}{\mathrm{(M\cdot n\cdot L)^{\oplus}B^{\ominus}}}$$

$$\mathrm{M = Li, Na, K;\quad B = OH, OR, NR_2;\quad L = Me_2S \rightarrow 0\ (DMSO),}$$
$$\mathrm{(Me_2N)_3P \rightarrow 0\ (HMPA),\ Alk_3P \rightarrow 0,\ NH_3,\ crown\ ethers,\ cryptands,\ etc.}$$

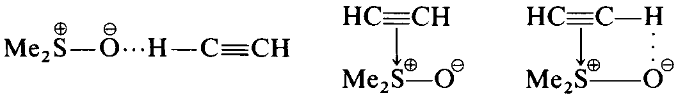
Another important feature of superbasic systems is a very low proton activity due to weak autoprotolysis, a small concentration of a proton transfer agent (when it is needed), and its immobilization by very strong hydrogen bonding.

In such systems the base strength is sharply enhanced (by seven or more powers of ten[7]) as is the free energy and nucleophilicy of the anions[8] which are becoming supernucleophiles ready to smoothly add across a triple bond.

Base: 0·025 M $NaOCH_3$

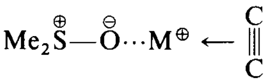
Solvent	Acidity function, H_-
methanol	12·2
95% DMSO + 5% methanol	19·4

In these systems acetylene can be activated in at least three ways. These are specific interaction and complexation with the solvent:



$$Me_2\overset{\oplus}{S}-\overset{\ominus}{O}\cdots H-C\equiv CH \qquad \begin{array}{c} HC\equiv CH \\ \downarrow \\ Me_2\overset{\oplus}{S}-O^{\ominus} \end{array} \qquad \begin{array}{c} HC\equiv C-H \\ \downarrow \qquad \vdots \\ Me_2\overset{\oplus}{S}-\!\!-O^{\ominus} \end{array}$$

incorporation into the inner solvation sphere of the metal cation:



$$Me_2\overset{\oplus}{S}-\overset{\ominus}{O}\cdots M^{\oplus} \longleftarrow \begin{array}{c} C \\ ||| \\ C \end{array}$$

and ionization and formation of acetylides:

$$K^{\oplus}B^{\ominus} + HC\equiv CH \rightleftharpoons BH + K^{\oplus} \qquad {}^{\ominus}C\equiv CH$$

Our **ab initio** (STO-4GF) study[9] shows that the acetylene-alkali metal cation interaction is really binding, and the complexes formed have a non-classical bridged structure in which the electron density is transferred to the cation so that the lowest vacant molecular orbitals of the coordinated acetylene lie at a lower energy level than those of free acetylene and therefore the triple bond becomes more sensitive to nucleophilic attack.

Complexing energy, Kcal/mol

M	$\overset{M^{\oplus}}{\dot{C}\equiv\dot{C}}$	$M-C=C^{\oplus}$
Li	39.3	22.0
Na	15.9	−10.0

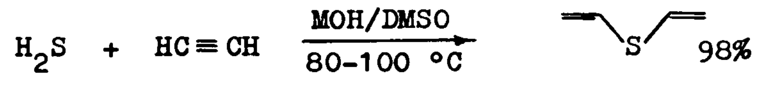
Electron density transfer to M^+

M	$\overset{M^{\oplus}}{\dot{C}\equiv\dot{C}}$	$M-C=C^{\oplus}$
Li	0.31	0.38
Na	0.08	0.10

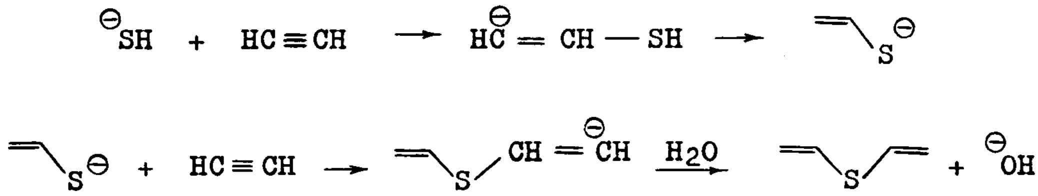
III. REACTIONS OF SULFUR NUCLEOPHILES WITH ACETYLENE IN SUPERBASIC MEDIA

1. Sulfide ions

In certain superbasic media, the simplest sulfur nucleophiles (sulfide and hydrosulfide ions) readily react with acetylene under mild conditions (80–100 °C, atmospheric or slightly higher pressure) to form divinyl sulfide[10] in nearly quantitative yield (under optimum conditions).



This is conventionally depicted as a subsequent addition of the sulfide ions to two moles of acetylene; however, all attempts to unambiguously trap the intermediate vinyl thioanion or to stop the reaction after this first step have failed as yet, implying a concerted one-step mechanism.



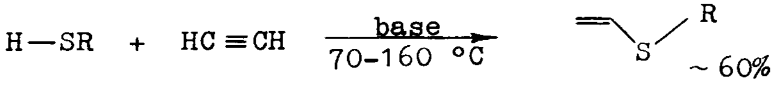
As follows from the conventional equilibrium:

$$H_2S + 2^{\ominus}\,OH \rightleftharpoons {}^{\ominus}SH + {}^{\ominus}OH + H_2O \rightleftharpoons S^{2\ominus} + 2H_2O$$

$$H_2S,\ M_2S,\ MSH;\ M = Li, Na, K$$

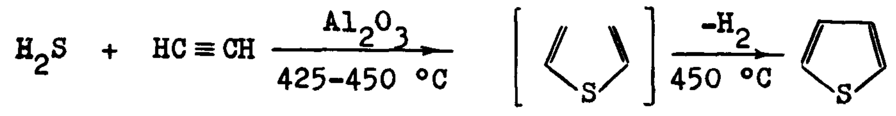
the sulfide ions can be generated with equal ease from hydrogen sulfide or alkali metal sulfides and hydrosulfides. Sodium sulfide proves to be the more convenient reagent in small-scale and lab syntheses where no problems emerge with waste sodium hydroxide contaminated with sulfides, whilst the hydrogen sulfide-based process seems to be more attractive for industrial use since it is of a catalytic nature and, once initiated, requires nothing but hydrogen sulfide and acetylene and, when optimized, operates with no waste whatsoever.

Now one may be surprised why such a rather obvious and predictable reaction was not carried out in practice recently in spite of the long-lasting and widespread synthetic and theoretical exploration of the addition of thiols to the triple bond.[11,12]



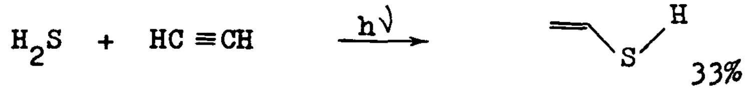
R - organic radical, but not hydrogen

In fact, the high-temperature alumina catalyzed reaction between hydrogen sulfide and acetylene affording thiophene was explored by Chichibabin as early as the beginning of this century.[13]

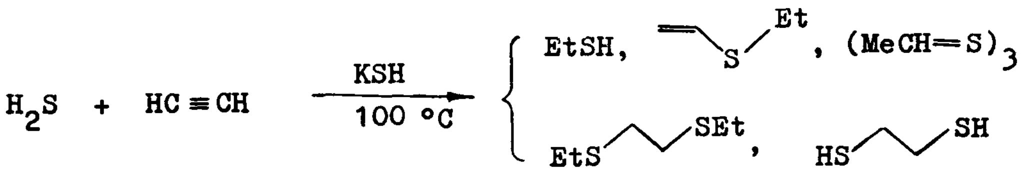


But only today it becomes clear why divinyl sulfide could not be prepared under these conditions. As was recently shown by Voronkov *et al.*, at a temperature higher than 400 °C divinyl sulfide undergoes dehydrogenation to thiophene.[14]

Photochemical addition of hydrogen sulfide to acetylene has been found to give the unstable vinyl mercaptan.[15]



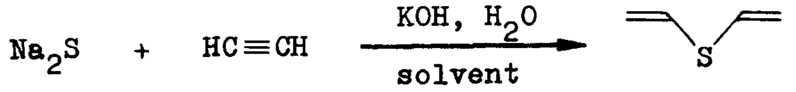
However, particularly astounding seem the results of Reppe's attempts to add hydrogen sulfide to acetylene in the presence of potassium hydrosulfide. A complex mixture of different organic sulfur compounds including ethanethiol, ethyl vinyl sulfide, 1,2-di(ethylthio)ethane, 1,2-ethanedithiol and trimeric thioacetaldehyde, but not divinyl sulfide, were obtained in this case.[16]



The following table gives the answer to this puzzle. It can be seen that positive results can be attained only using dipolar aprotic solvents in which superbasic media are formed

TABLE

Influence of the Solvent on the Yield of Divinyl Sulfide in the Reaction[a]

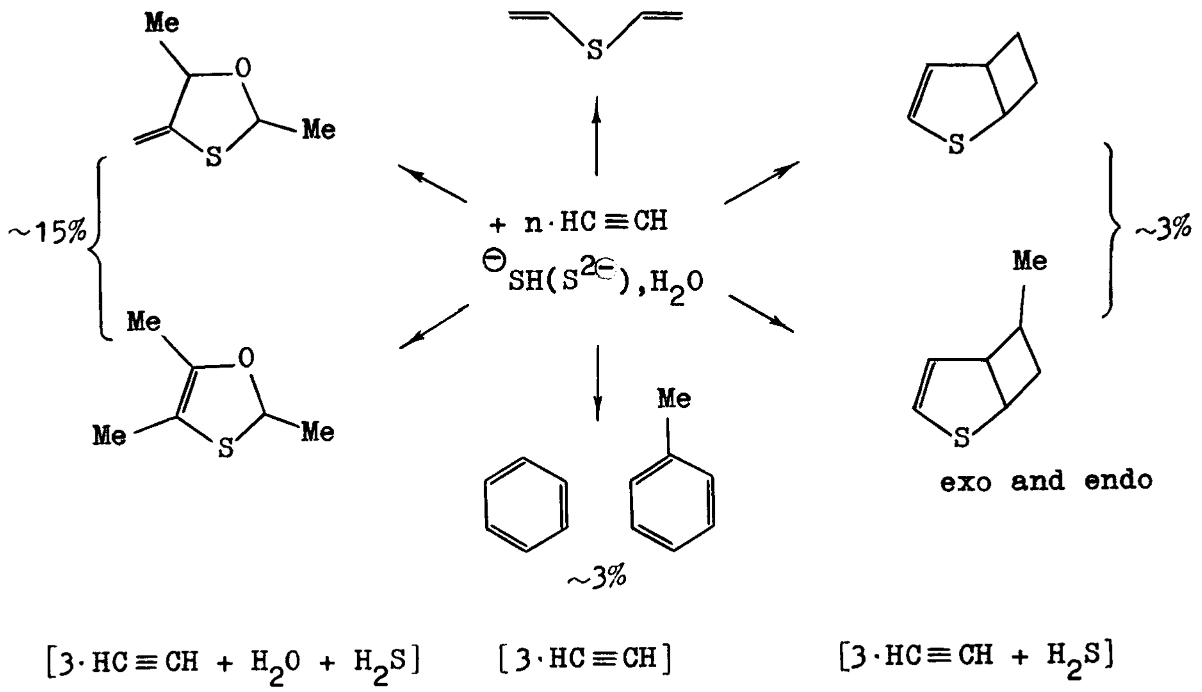


Solvent	Yield, %
DMSO	80
HMPA	40
Sulfolane	20
Water	5
DMF	traces
TGF	traces
Acetone	traces

[a] Reaction conditions (not optimized): 100–110 °C, autoclave, initial C_2H_2 pressure 12 atm, KOH 15 mass %, H_2O 10 mass % relative to solvent.

SCHEME I

Cyclooligomerization of acetylene with sulfide ions in the NaOH-DMSO-H_2O system, 80-100 °C

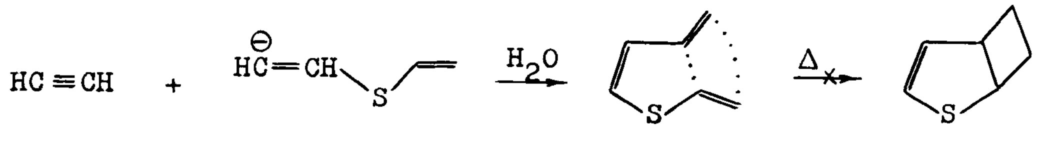


and the abovementioned specific activation of sulfide ions and acetylene takes place. The best solvent for the synthesis of divinyl sulfide found so far is dimethyl sulfoxide.

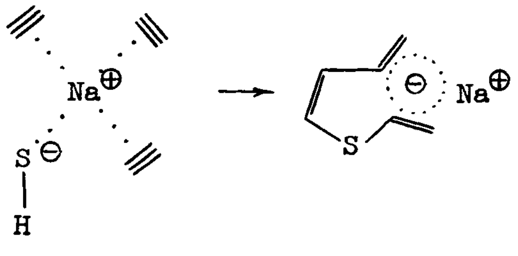
In some superbasic media the simple addition of sulfide ions to acetylene takes place concurrent with unusual cyclooligomerization reactions (Scheme I).

For instance, in the system NaOH-DMSO-H_2O, besides divinyl sulfide, there are formed 2,5-dimethyl-4-methylene-1,3-oxathiolane and its endocyclic isomer 2,4,5-trimethyl-1,3-oxathiol, formed from three molecules of acetylene, one molecule of hydrogen sulfide and one molecule of water.[5,6] From the reaction mixture there were also isolated three bridged sulfur-containing heterocycles—2-thiabicyclo[3.2.0]-3-heptene and its *exo*- and *endo*-6-methyl substituted derivatives which are built of three molecules of acetylene and one molecule of hydrogen sulfide.[5,17] Benzene and toluene were also detected among the reaction products. The methylation seen here is due to the presence of dimethyl sulfoxide.

It is difficult to explain the formation of these sulfur containing cyclooligomers by subsequent additions because of the absence in the reaction mixture of any isolable intermediates and the improbability of their thermal [2 + 2] cyclization.



On the basis of our recent **ab initio** study[18,19] which predicts the coordination of two or three molecules of acetylene to the sodium or potassium cations we have suggested a one-step template cyclization which gives the key to the understanding of the formation of all the above products, including benzene and toluene.



Scheme II shows one of the possible solvation templates in the system consisting of sodium hydrosulfide, acetylene, dimethyl sulfoxide, and a small amount of water.

Regardless of the modest and low yields of these heterocycles their one-pot formation from very cheap raw materials makes them readily accessible for synthetic application.

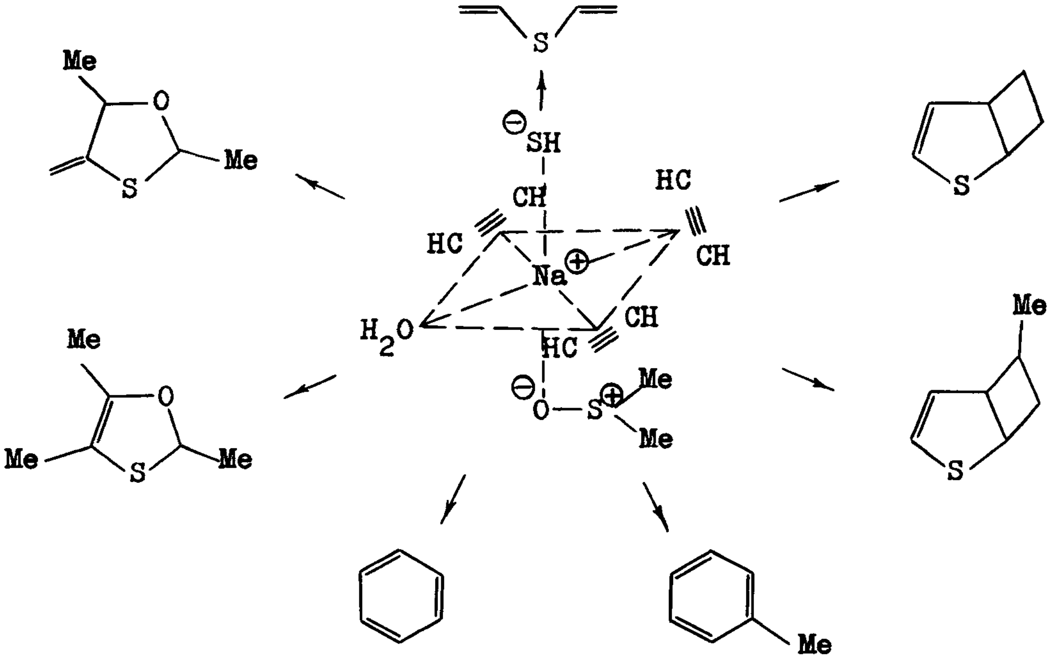
Here we apparently encounter coordination catalysis of a new type, intermediate between solvated cations and stable metal complexes.

These superbasic catalytic systems display one more feature germane to typical metal complex catalysis: it is the fact that the direction of the synthesis often profoundly depends on the nature of the ligands. Thus, if DMSO is replaced by HMPA, then in the

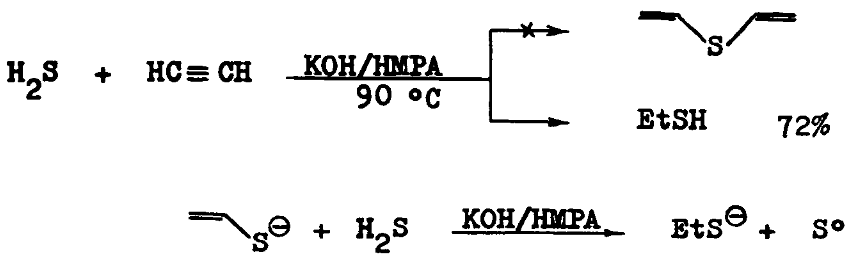
SCHEME II

One of possible solvation templates in the system

NaSH - HC≡CH - DMSO - H_2O



reaction of hydrogen sulfide with acetylene it is possible to find conditions in which ethanethiol is the only product instead of divinyl sulfide.[5]

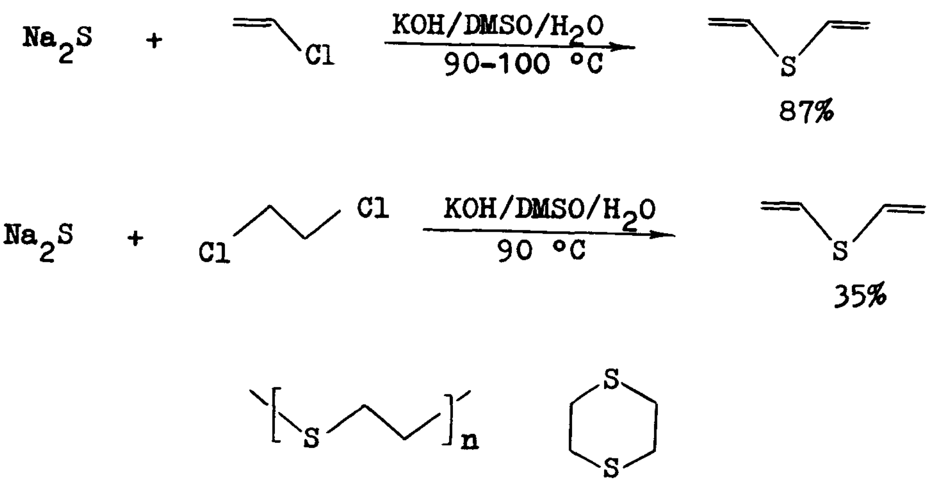


This synthesis is, perhaps, not so much of preparative as of principal value because it clearly indicates the capability of certain superbases to promote redox reactions of sulfur compounds. The reduction of the intermediate vinyl thioanion during this interaction of hydrogen sulfide and acetylene in the KOH-HMPA system is in keeping with Russel's observations that the basic HMPA is a much more efficient reducing agent than the basic DMSO.[20]

Some acetylenic synthons (cryptoacetylenes) such as vinyl halides or dihaloethanes (Scheme III) can be utilized satisfactorily instead of free acetylene in the synthesis of divinyl sulfide from sodium sulfide.[21,22] It is interesting to note that while poly(ethylene sulfide) and 1,4-dithiane are conventional products of the latter reaction, they are practically not formed in the system KOH-DMSO.

SCHEME III

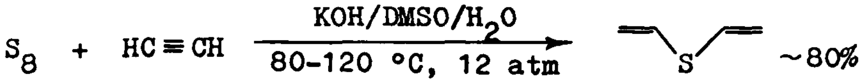
Divinyl sulfide from Na_2S and vinyl halides or dihaloethanes



small amounts

2. Elemental sulfur (selenium, tellurium)

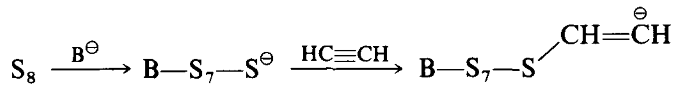
In superbasic solutions containing DMSO or HMPA the cyclooctasulfur is readily cleaved at 80–120 °C to form with acetylene the same products as in the case of sulfide ions.



This is chiefly divinyl sulfide which can be obtained by this reaction in a yield up to 80 %[5,6,23], assuming that two sulfur equivalents give one equivalent of sulfide ion.

$$1/2\,S_8 + 4\,{}^{\ominus}OH \longrightarrow 2\,HS^{\ominus} + S_2O_3^{2\ominus} + H_2O$$

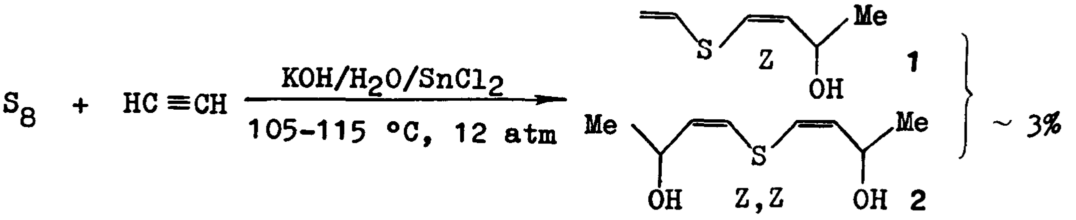
However, the anions attacking the triple bond initially are apparently not monosulfides, but polysulfides originating from the base-induced ring opening of the sulfur octamer which have a higher nucleophilicity.



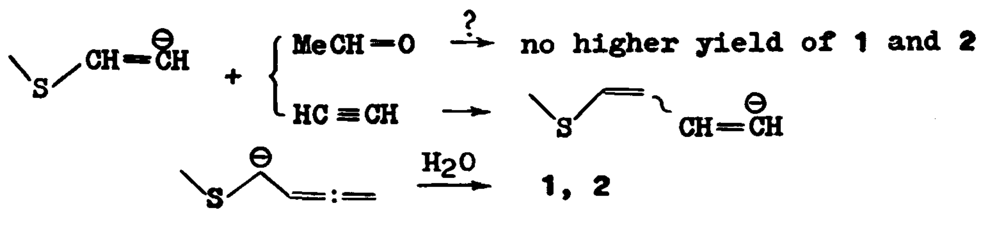
$$S_8 \xrightarrow{B^\ominus} B{-}S_7{-}S^\ominus \xrightarrow{HC\equiv CH} B{-}S_7{-}S{-}CH{=}\overset{\ominus}{C}H$$

This two-step cleavage-addition process can possibly proceed with simultaneous electrophilic assistance by the acetylene molecule. Further extrusion of sulfur atoms from the initial adducts leads then to divinyl sulfide as the most stable product under these conditions.

If this reaction is carried out without DMSO or HMPA in aqueous potassium hydroxide in the presence of tin(II) chloride as a reducing agent, only traces of divinyl sulfide can be detected in the mixture of products from which *Z*-1-vinylthio-3-hydroxy-1-butene (**1**) and *Z*,*Z*-bis(3-hydroxy-1-butenyl) sulfide (**2**) were isolated in a total yield of about 3%[24]; no attempts to optimize this unpredictable reaction have been made so far.



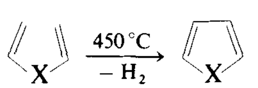
These two substituted divinyl sulfides **1**, **2** could be expected to result by trapping of the intermediate vinyl thiocarbanions either by acetaldehyde, a probable product of the hydration of acetylene, or by acetylene itself. However, no increase in the yield of these hydroxydivinyl sulfides was observed when acetaldehyde was added to the reaction mixture. In the case where the initial carbanion is trapped by acetylene, the most stable anion which can be formed should have the structure of a terminal allene with the charge in the α-position relative to the sulfur. In the presence of water such an intermediate may afford the above mentioned hydroxydivinyl sulfides **1**, **2**.



But it is not clear why this transformation should be stereospecific as is the case in this experiment. The stereospecifity observed implies again a coordination mechanism operating in the solvation shell of the potassium cation. Nevertheless, the detailed course of this unusual reaction is still far from understood.

In analogy with sulfur, elemental selenium and tellurium were found to undergo reaction with acetylene in the systems KOH-HMPA-H_2O[5] or KOH-H_2O-tin(II) chloride to afford divinyl chalcogenides and their hydroxyethyl derivatives[25] as well as selenophene and tellurophene. The yields and ratio of these products strongly depend on the reaction conditions (temperature, duration, acetylene pressure, nature and proportions of reagents, etc.). The best yields obtained so far are as follows: divinyl selenide: 75 % (assuming that in the absence of a special reductant three equivalents of selenium give two equivalents of selenide ions), divinyl telluride: 92 % (based on the whole amount of tellurium, since $SnCl_2$ was used as a reduction), *Z*-1-vinylseleno-3-hydroxy-1-butene: 54 %, selenophene: about 20 %, and other products: not higher than 5 % (Scheme IV).

Selenophene and tellurophene are now becoming available via high temperature dehydrocyclization of the corresponding divinyl chalcogenides.[26]

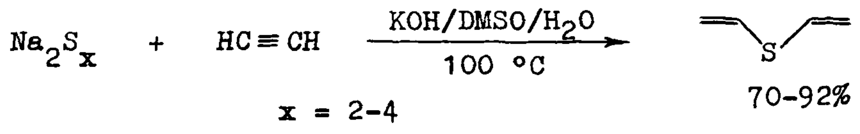


X = Se(50 %), Te(76 %)

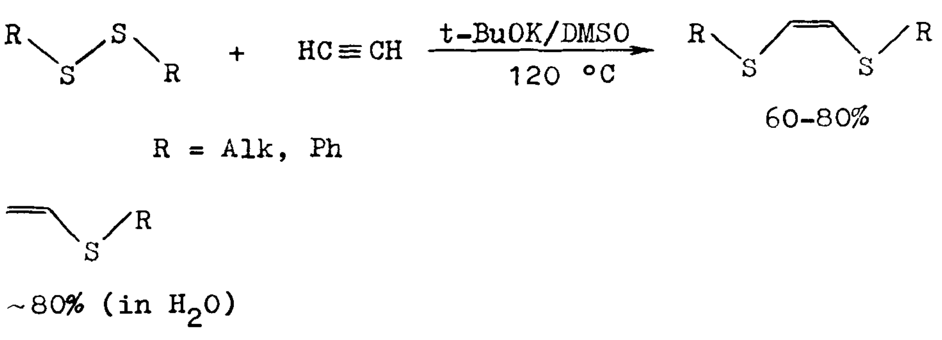
One can see that the ease of these chalcogen-acetylene reactions increases from sulfur to tellurium in keeping with the higher nucleophilicy of the havier chalcogen anions.

3. *Di- and polysulfides*

Closely related to these autoredox processes are reactions between alkali metal polysulfides and acetylene in the same superbasic systems, proceeding with a similar cleavage of the S—S bonds to afford divinyl sulfide in 70–90 % yield.[5]

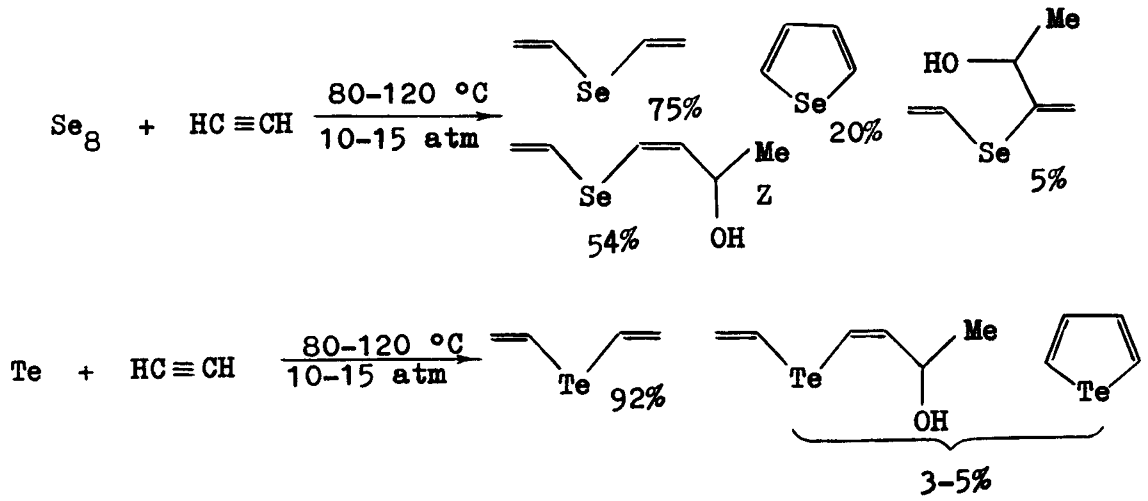


In the case of organic disulfides, acetylene readily inserts into the S—S bond to give *Z*-1,2-di(organothio)ethenes in a 60–80 % yield.[5] If there are favorable conditions for proton transfer (say, a considerable amount of water in the reaction mixture), then alkyl vinyl sulfides are formed as well, the yield of which can be as high as 80 %.[5]

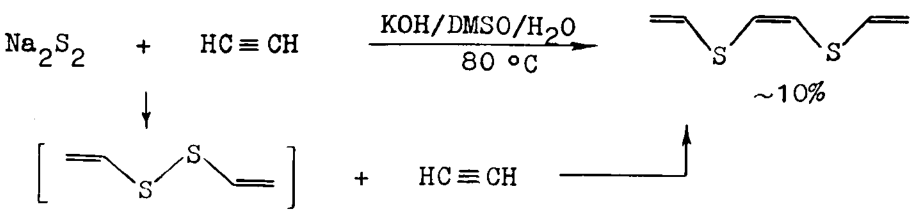


SCHEME IV

Reactions of selenium and tellurium with acetylene in the systems $KOH-HMPA-H_2O$ and $KOH-H_2O-SnCl_2$

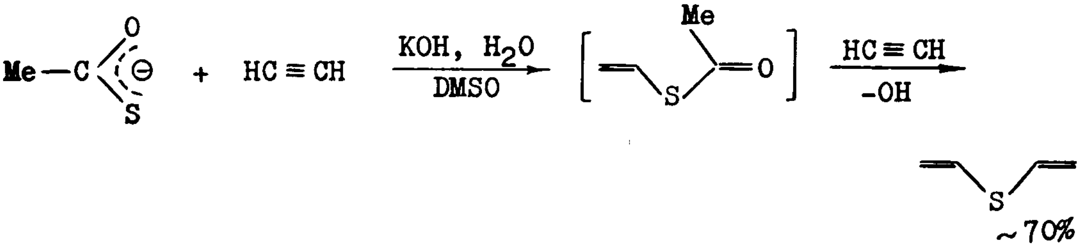


The facile cleavage of the S—S bond under these conditions makes the synthesis of divinyl polysulfides difficult. However, they seem nevertheless to form as intermediates. This is evident regarding a 1,2-di(vinylthio)ethene preparation from sodium disulfide and acetylene.[5]

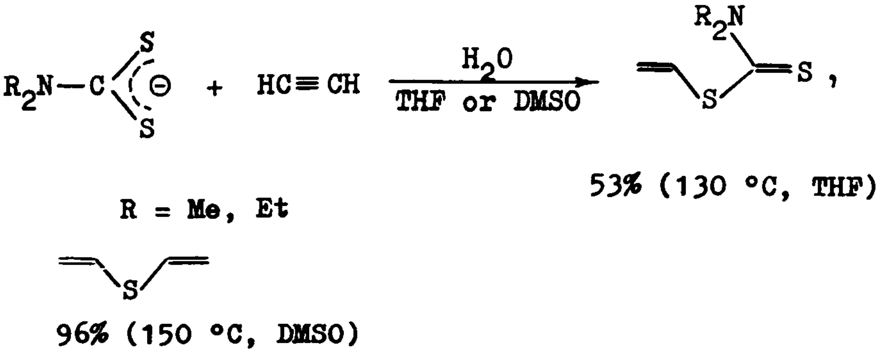


4. *Thioacid anions and thione systems*

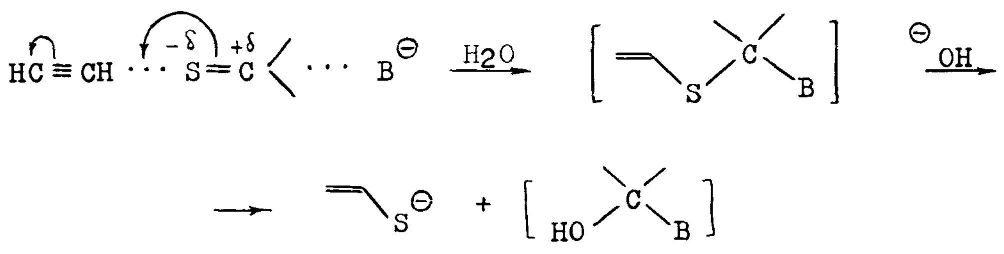
The reactions of thiocarboxylic and thiocarbonic acid salts with acetylene in the presence of an appropriate amount of a proton donor provide another new source of vinylic sulfur compounds. Such a weak nucleophile as the thioacetate anion, previously considered incapable of interacting with acetylene, readily does so in the system KOH-DMSO.

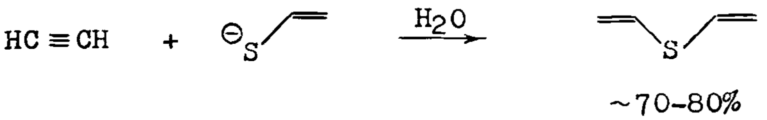


The adduct, vinyl thioacetate, in the presence of KOH of increasing concentration, particularly in DMSO, is not stable, and readily suffers alkaline breakdown to form, with excess acetylene, divinyl sulfide in about 70 % yield.[27] At the same time, in some cases such reactions can be stopped at the addition stage to yield the expected *S*-vinyl ester. So, in this way, when DMSO was replaced by tetrahydrofuran (THF), *N*,*N*-dialkyl-*S*-vinyl dithiocarbamate could be synthesized in satisfactory yield (53 %), whilst in the former solvent divinyl sulfide is formed almost quantitatively.[28]

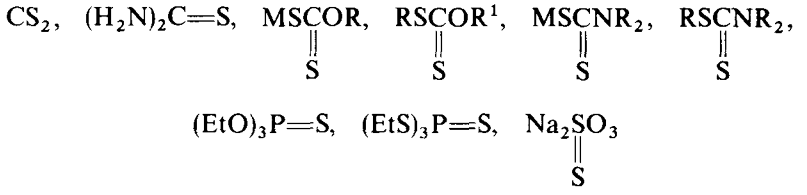


Under the influence of superbases unconventional reactions between thione systems and acetylene occur easily.





Thione systems already shown to be involved in such interactions include the following: carbon disulfide,[5] thiourea,[29,30] esters, amides, and salts of thiocarbonic[31] and thiophosphorus[32] acids, and sodium thiosulfate.[5]



$$CS_2,\ (H_2N)_2C{=}S,\ MS\underset{\underset{S}{\|}}{C}OR,\ RS\underset{\underset{S}{\|}}{C}OR^1,\ MS\underset{\underset{S}{\|}}{C}NR_2,\ RS\underset{\underset{S}{\|}}{C}NR_2,$$

$$(EtO)_3P{=}S,\ (EtS)_3P{=}S,\ Na_2\underset{\underset{S}{\|}}{S}O_3$$

Owing to its high polarizability the thione group behaves in the presence of a strong base as an active uncharged nucleophile. In the course of a series of consecutive or simultaneous additions and substitutions divinyl sulfide is usually formed (yields are within 70–80 %).

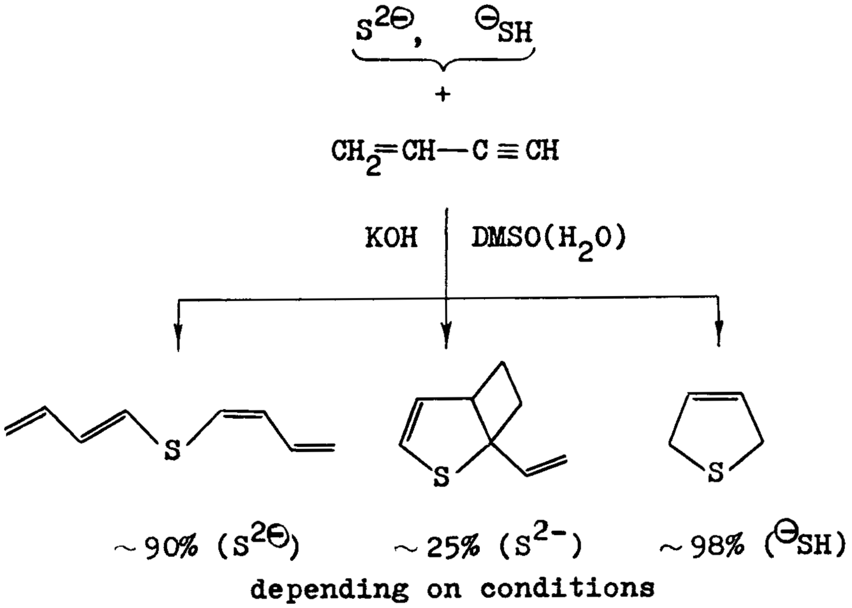
IV. REACTIONS OF SUBSTITUTED ACETYLENES WITH CHALCOGEN NUCLEOPHILES IN SUPERBASIC MEDIA

Almost all reactions discussed are of a rather general character and not only possible with acetylene itself but with substituted acetylenes as well. For example, vinylacetylene interacting with activated sulfide ions gives di-1-(1,3-butadienyl) sulfide into a yield exceeding 90 %.[33] Changing the reaction conditions leads to heterocyclization either 1-vinyl-2-thiabicyclo[3.2.0]-3-heptene or dihydrothiophene which hitherto were almost inaccessible (Scheme V). This way dihydrothiophene can be synthesized in practically quantitative yield.

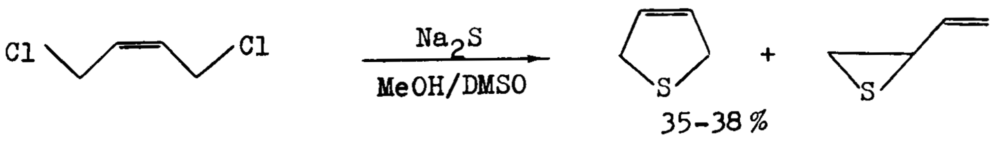
Until recently the best method for the preparation of 2,5-dihydrothiophene was considered to be one based on the reaction of 1,4-dichloro-2-butene with sodium sulfide

SCHEME V

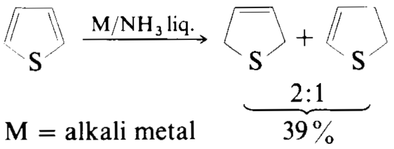
Reactions of sulfide ions with vinylacetylene



in a methanol-DMSO mixture affording dihydrothiophene in a yield of 35–38 % along with 3,4-epithio-1-butene.[34]

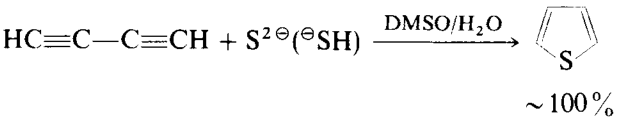


Earlier there was but one method for preparation of 2,5-dihydrothiophene—partial reduction of thiophene with alkali metals in liquid ammonia,[35] the product being isolated either by careful fractional distillation of a 1:2 mixture (39 % yield) of 2,3- and 2,5-isomers or by acid hydrolysis of the former.

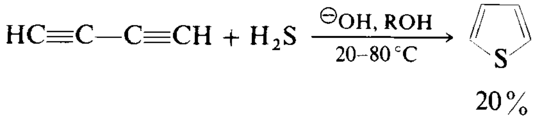


Using vinylacetylene and elemental selenium or tellurium in superbasic media (Scheme VI) direct syntheses of selenophene, di-1-(1,3-butadienyl) selenide,[36] di-1-(1,3-butadienyl) telluride, 1-vinyl-2-selenobicyclo [3.2.0]-3-heptene as well as of methyl 1-(1,3-butadienyl) selenide and methylthiomethyl 1-(1,3-butadienyl) selenide have been achieved, the latter two being formed with the participation of DMSO.[37]

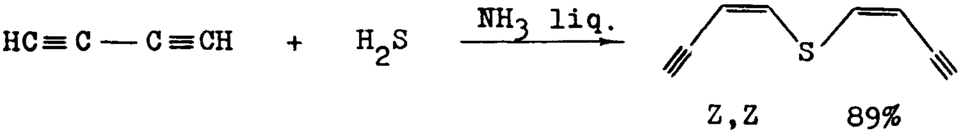
Diacetylene reacts very smoothly with sodium sulfide in slightly aqueous DMSO or with hydrogen sulfide in the system KOH-DMSO to give thiophene of high purity in nearly quantitative yield.[38,39]



These reactions seem to have a good chance to be adopted by industry because of a certain technical demand for thiophene and an acute need to utilize diacetylene, a multi-tonnage by-product of acetylene production by pyrolysis of hydrocarbons. The earlier diacetylene-based synthesis of thiophene is known to give yields no higher than 20 %[40] and, consequently, did not attract much attention in either industrial or preparative chemistry.



When diacetylene and sulfide ions interact in liquid ammonia, *Z*,*Z*-di-1-(1-buten-3-ynyl) sulfide is formed in about 90 % yield.[41]



The reaction of phenylacetylene with sulfide or thioacetate anions under phase transfer conditions (Scheme VII) appears to be one of the first examples of the operation of Makosza's interphase catalysis[42] to accelerate nucleophilic addition across a triple bond.[43]

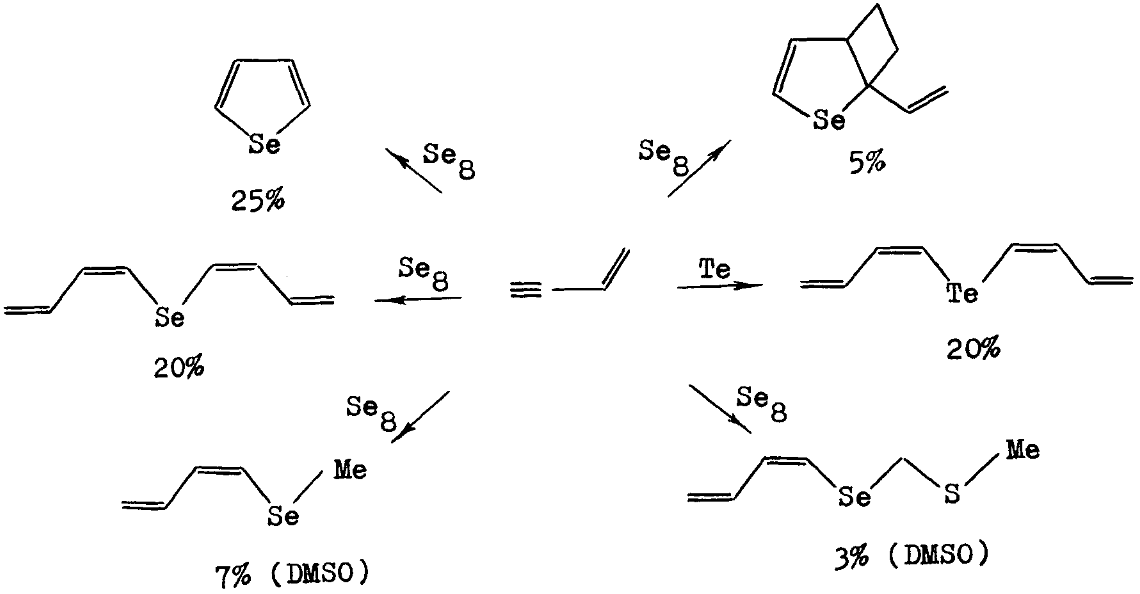
The best yields of di(2-phenylvinyl) sulfide have been obtained with crown ether (dibenzo-18-crown-6) as a catalyst whereas with a quaternary ammonium salt (triethylbenzylammonium chloride) the yields were only half as much.

V. SOME PROSPECTIVE APPLICATIONS

Thus, one can see (Scheme VIII) that a set of new monomers, chemicals and synthons is now becoming available owing to the above reactions of sulfur and its simple compounds

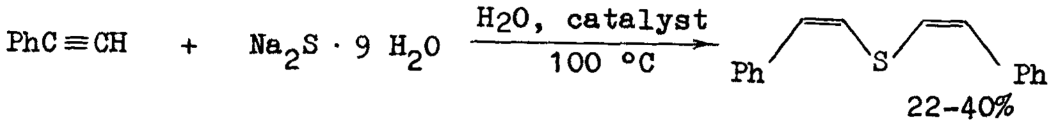
SCHEME VI

Unsaturated chalcogenides from elemental chalcogens and vinylacetylene in the systems KOH-HMPA-H_2O and KOH-DMSO-H_2O, 110-120 °C

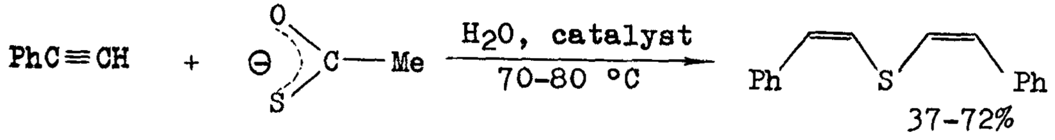


SCHEME VII

Phase transfer addition of some thio-anions to phenylacetylene



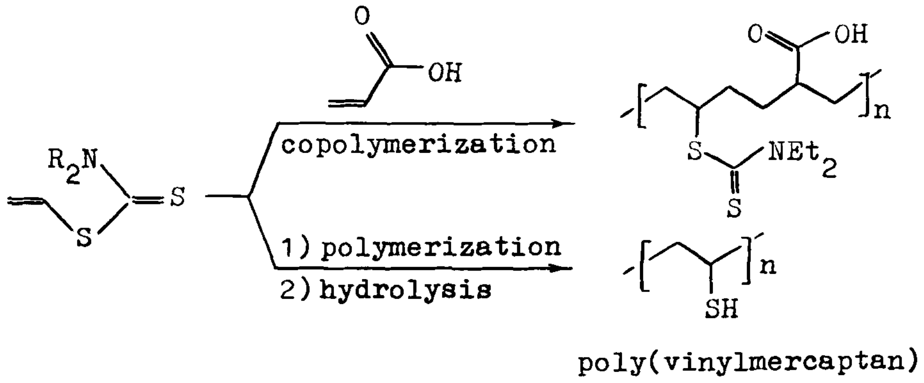
Catalyst	Crown ether	TEBA	None
Yield, %	40	22	9



Catalyst	Crown ether	TEBA	None
Yield, %	72	37	0

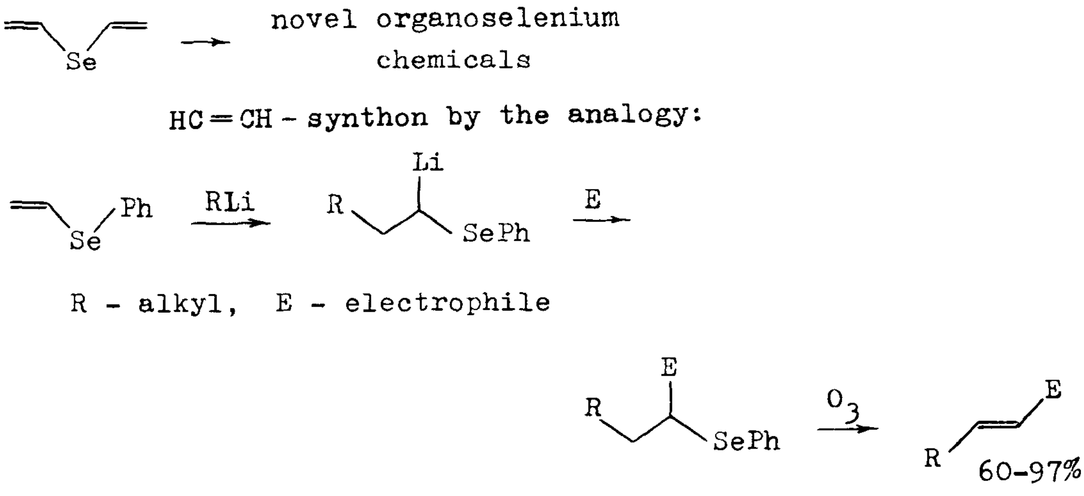
as well as of elemental selenium and tellurium with acetylene and its derivatives in superbasic media.

Some of these compounds are already underway to interesting applications. For example, it has recently been found that copolymers of *S*-vinyl dithiocarbamates and acrylic acid exhibit radioprotective activity.[44]



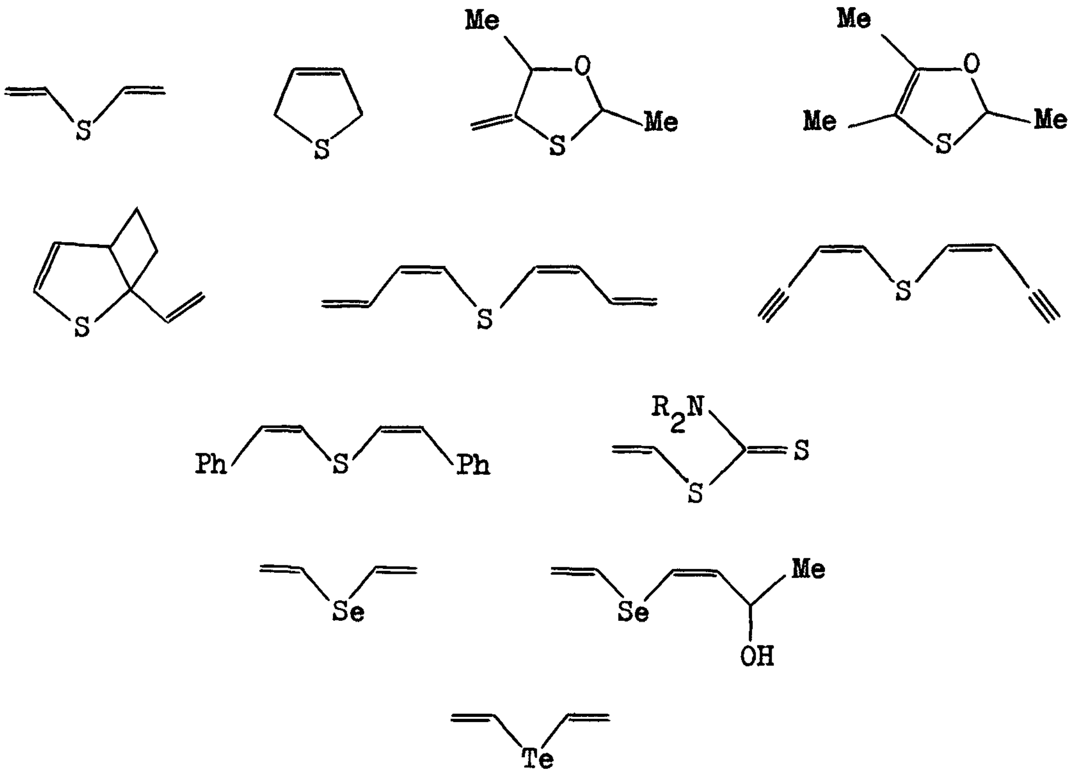
Such copolymers are expected to be free of a main disadvantage of protective agents of low molecular mass, i.e. the short duration of their action due to rapid metabolism and excretion. Besides, these monomers are good precursors for poly-(vinylmercaptan), a very promising redox, ion-exchange, and complexing polymer.

Divinyl selenide now attracts attention as a new and productive source of novel organoselenium compounds as well as a useful CH=CH synthon replacing the less accessible phenyl vinyl selenide[45] proposed for this purpose according to the following sequence: reaction with alkyllithiums, trapping of the resulting α-lithioalkyl selenides with electrophiles and oxidative elimination of benzeneselenic acid to produce the disubstituted alkenes.

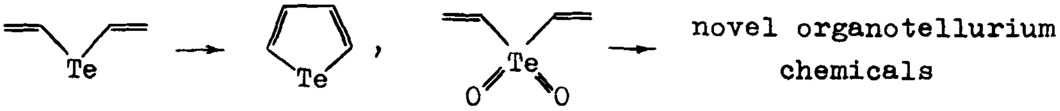


SCHEME VIII

New acetylene based sulfur, selenium and tellurium chemicals



Likewise, divinyl telluride is a perspective key compound for the preparation of novel organotellurium materials, in particular bearing in mind that today organotellurium chemistry is an active area of research for applications in dry non-silver imaging processes.[46]



1. Divinyl sulfide, a synthon and monomer

However, among all the above compounds (Scheme VIII) it is divinyl sulfide that has been provoking most research efforts after new acetylene-based methods for its preparation have been developed.

Perhaps it might be of interest to recall that divinyl sulfide was discovered almost a century ago and not as a synthetic compound, but as a component of the essential oil of the leek, **Allium ursinum L.**[47] Much later (1952), divinyl sulfide was isolated from another plant, the onion **Allium sativum**, along with allyl vinyl sulfoxide and their co-oligomers which happen to possess strong bactericidal activity.[48]

Nowadays, divinyl sulfide is under increasing synthetic investigation[49] where use is made of various reactions across its very reactive double bonds prone not only to common free-radical and electrophilic additions but also to a number of cycloadditions and even electrophilic substitutions.

These reactions give rise to new families of vinylic and cyclic functionalized sulfides with a wide scope of potential applications. Using bifunctional addends one may bring about polyaddition resulting in polysulfide oligomers.

Scheme IX shows typical reactions of divinyl sulfide with thiol compounds,[50] including organosilicon derivatives.[51] As a rule, these additions are regiospecific and give anti-Markovnikov adducts indicating a homolytic addition mechanism. However, the stronger the acidity of the addend the more the regiospecifity is weakened, implying the involvement of an electrophilic mechanism. Contrary to an earlier patent claim,[52] dimethyl dithiophosphoric acid with divinyl sulfide exclusively affords Markovnikov adducts.[50] In some cases, a second molecule of divinyl sulfide can take part in the addition, trapping the intermediate radical to form cyclic 2:1 adducts (substituted thiolanes and thianes). With dithiols thiokol-type polymers can be readily obtained.[49]

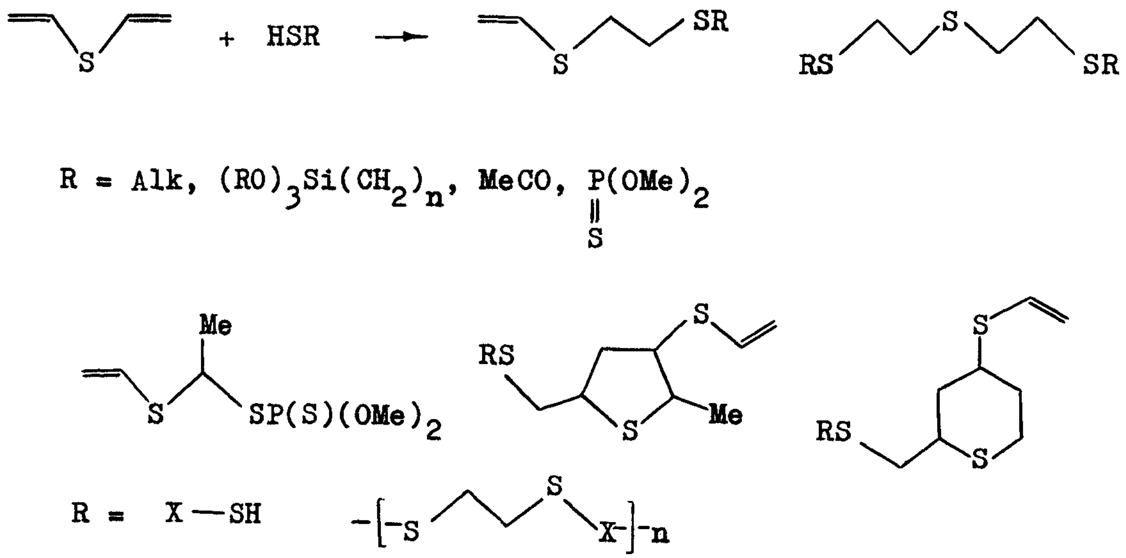
Presumably, the rather high toxicity (LD_{50} 110–170 $mg \cdot kg^{-1}$) of divinyl sulfide results from its ability to block thiol functions of enzymes.

Scheme X shows typical products of the hydrosilylation of divinyl sulfide.[53–56] Besides common α- and β-additions, C—S bond cleavage leading to vinylthiosilanes has been observed.[56] Correspondingly, with diethylsilane, four- and five-membered sulfur-silicon heterocycles have been isolated from the reaction mixture along with acyclic α- and β-addition products.[55]

Diels-Alder[57] and carbene[58] cycloadditions (Scheme XI) to divinyl sulfide provide 1:1 and 1:2 adducts,[49] potential monomers, biologically active compounds, and new synthetic intermediates.

SCHEME IX

Addition of thiol compounds to divinyl sulfide



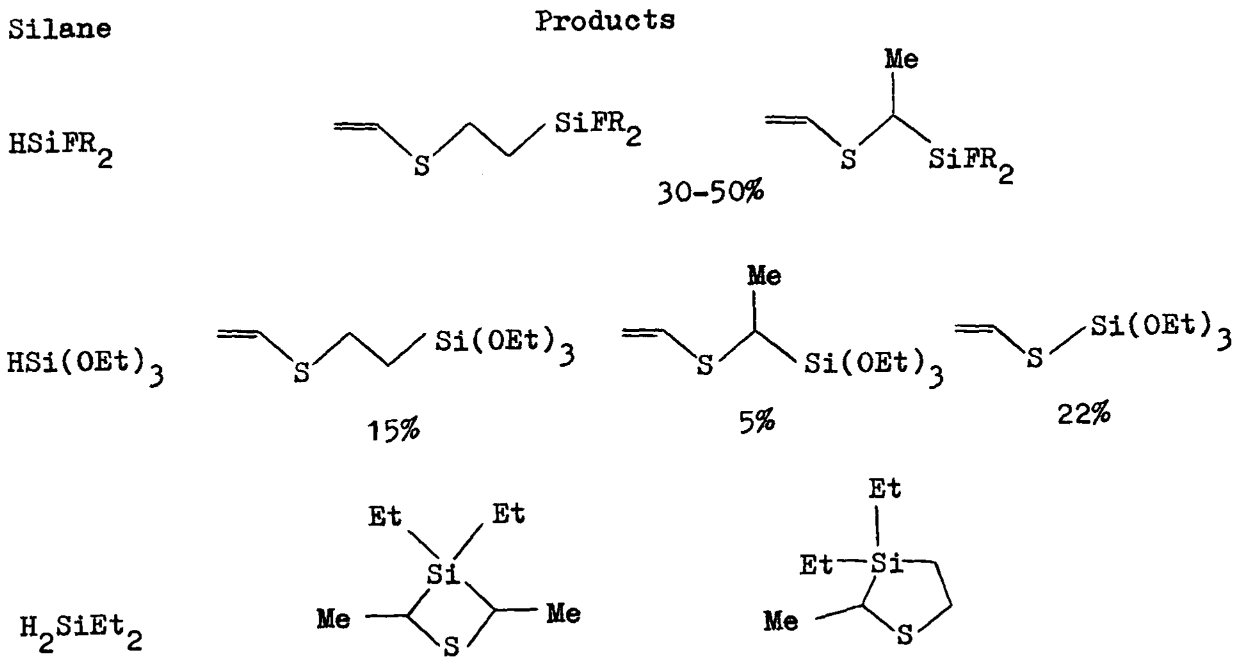
R = Alk, $(RO)_3Si(CH_2)_n$, MeCO, $\underset{\underset{S}{\|}}{P}(OMe)_2$

R = X—SH

X = H, $(CH_2)_2$, etc.

SCHEME X

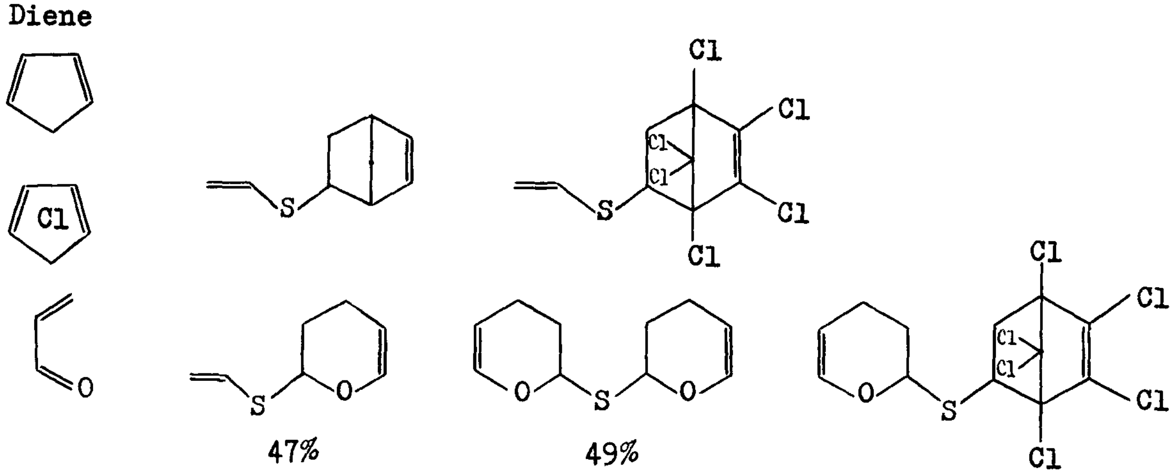
Typical products of hydrosilylation of divinyl sulfide



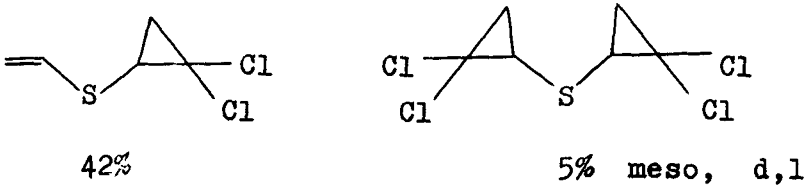
SCHEME XI

Typical cycloaddition products of divinyl sulfide

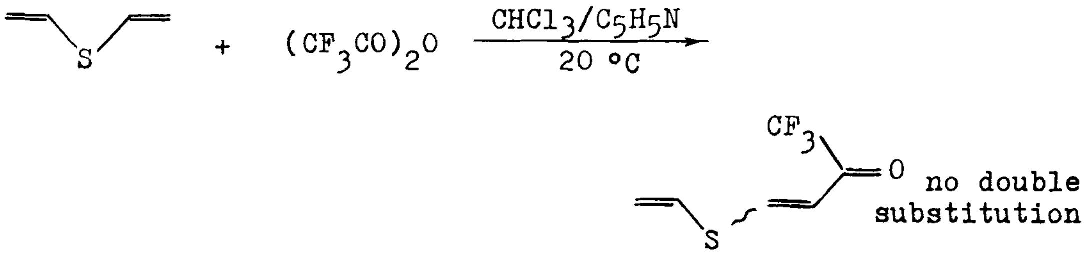
Diels - Alder additions



Halocarben additions



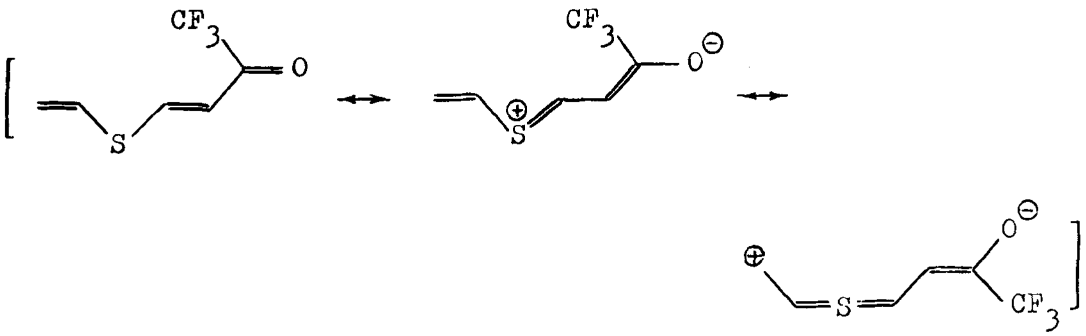
Under the action of trifluoroacetyl cations, one of the β-hydrogen atoms in divinyl sulfide is found susceptible to electrophilic substitution.[59] All attempts to bring about substitution of the second vinyl group were unsuccessful.



no double substitution

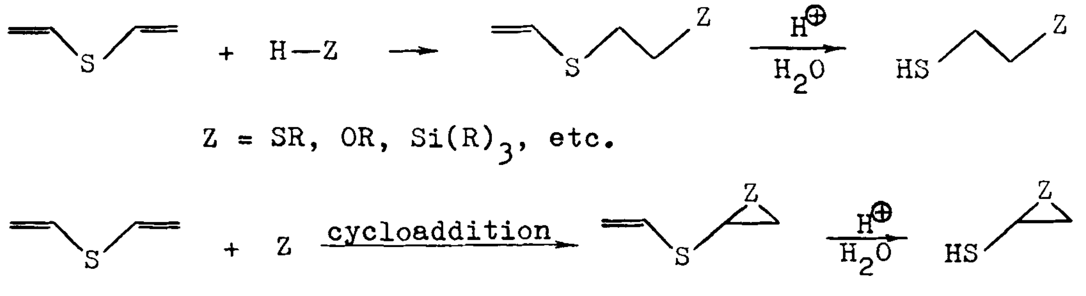
52% Z:E 1:2

The high selectivity of this process is explained by a profound change in the electronic nature of the remaining vinylthio group due to the effect of the trifluoroacetylvinyl substituent which involves the sulfur lone electron pair in a strong p-π-conjugation.

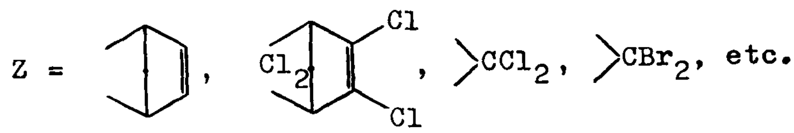


The so developed positive charge on the sulfur atom must make electron transfer to its vacant orbitals easier, thus further decreasing the nucleophilicity of the vinylthio group.

The known facility of the acid-catalyzed hydrolysis of a vinylthio group to release the thiol function, when combined with the above additions across one of its double bonds, makes divinyl sulfide a useful $HSCH_2CH_2$- and $HSCHCH_2$-synthon, according to the following general scheme:

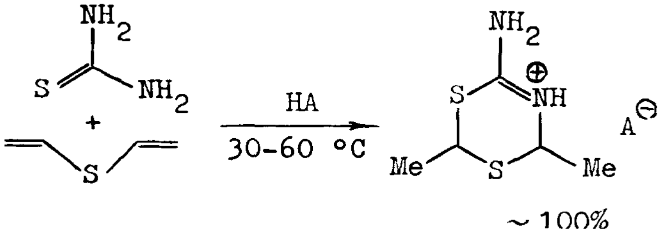


Z = SR, OR, $Si(R)_3$, etc.



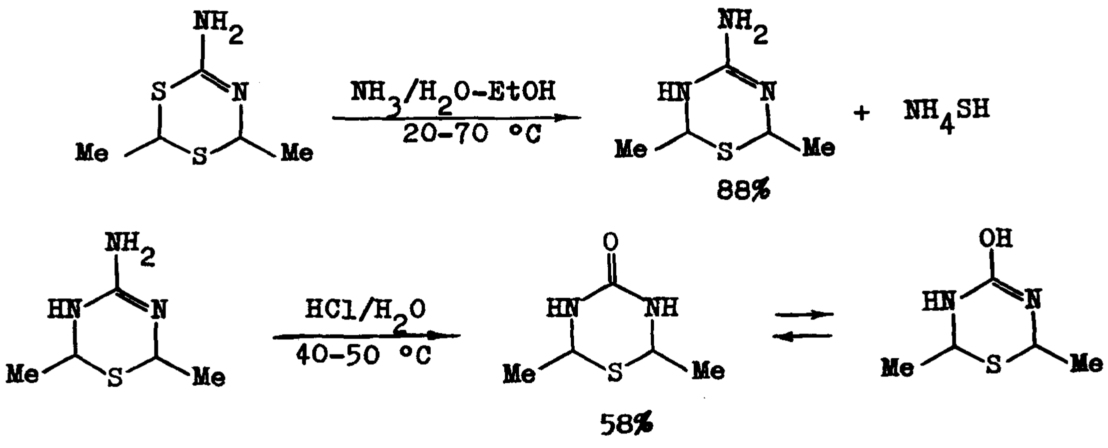
The synthetic potential of divinyl sulfide is still far from exhausted.

Recently, a cyclization under very mild conditions of divinyl sulfide with thiaurea which quantitatively affords 2-*H*,6-*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine has been found.[60–62]



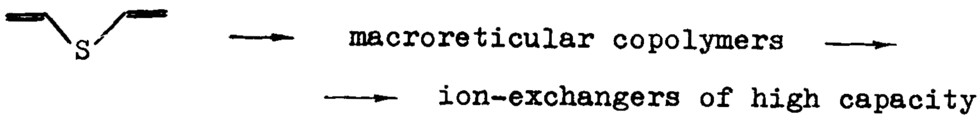
A = Cl, Br, ClO_4, NO_3

In aqueous-ethanolic ammonia the latter proved capable of exchanging readily its sulfur atom in position 5 for nitrogen to form the corresponding 1,3,5-thiadiazine,[63] which in turn can be converted into 1,3,5-thiadiazine-4-one under mild acid hydrolysis.

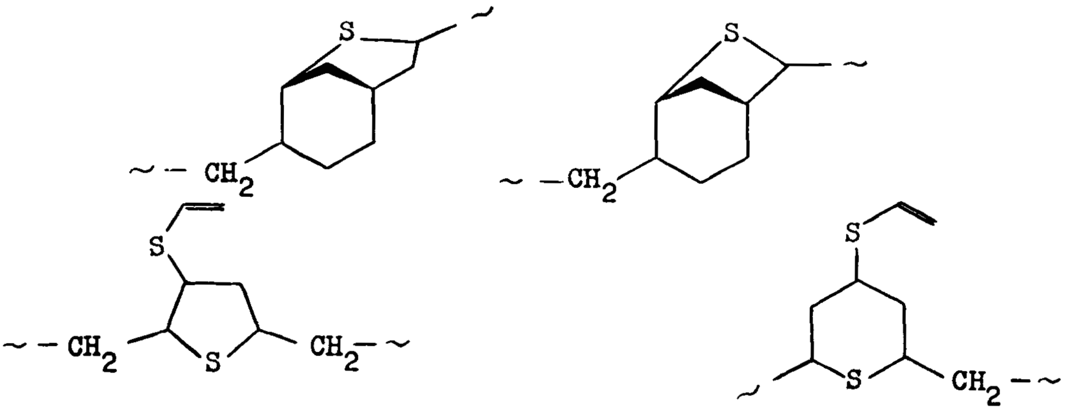


However, the most actively developing applications of divinyl sulfide are now in polymer chemistry.

As a cross-linking agent divinyl sulfide is known to give macroreticular structured copolymers.[49] Ion exchangers made from them possess an almost theoretical capacity and an ion exchange rate nearly as high as that of homogenous reactions.[49]



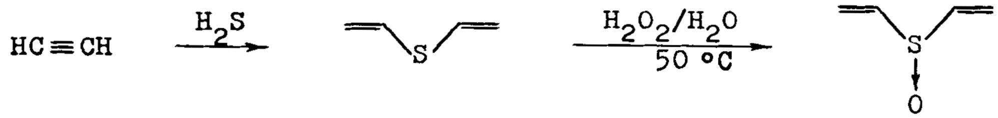
Divinyl sulfide has also been shown to undergo a bicyclic cyclopolymerization in the presence of free radicals producing soluble polymers the constitution of which mainly involves bicyclic structural units and minor amounts of monocyclic ones.[64]



Available vinylthio groups of the latter may be used for hardening and further modifications.

2. *Divinyl sulfoxide and its synthetic uses*

The above reaction of acetylene with sulfide ions to produce divinyl sulfide provides a two-step route from acetylene to divinyl sulfoxide, which, as such, is now growing into a technically feasible and commercially meaningful synthetic intermediate and monomer.[49]



Yield 90%

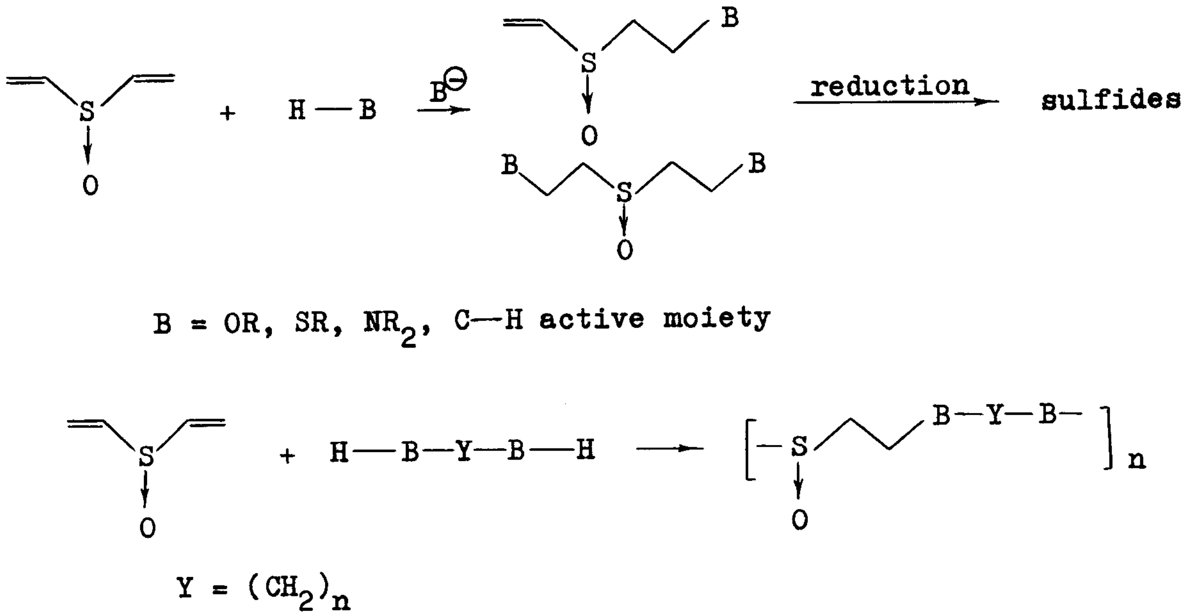
Purity 99,9% (after vacuum flashing)

In contrast to divinyl sulfide which is fully inert to nucleophiles, divinyl sulfoxide appears to be extremely active in Michael-like additions of many types (Scheme XII).

Various alcohols, thiols, amines, CH-acids and the like add to the double bonds of divinyl sulfoxide under rather mild conditions and nearly quantitative yields of the adducts can be achieved.[49] This makes accessible a practically unlimited number of novel

SCHEME XII

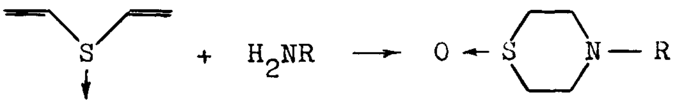
Nucleophilic additions to divinyl sulfoxide



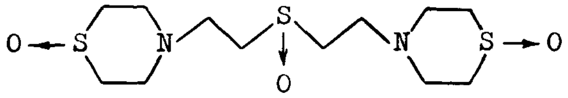
B = OR, SR, NR_2, C—H active moiety

Y = $(CH_2)_n$

functionalized sulfoxides as well as polymeric ones (if bifunctional addends are taken) suitable for a number of technical applications. This also seems to open the simplest way to a variety of functional sulfides via reduction of the sulfoxides obtained. The following reactions illustrate some possibilities for the synthesis of amino sulfoxides starting from divinyl sulfoxide. With ammonia the latter yields readily perhydrothiazine 1-oxide which therefore becomes now available as a parent intermediate to prepare many other *N*-substituted thiomorpholines.



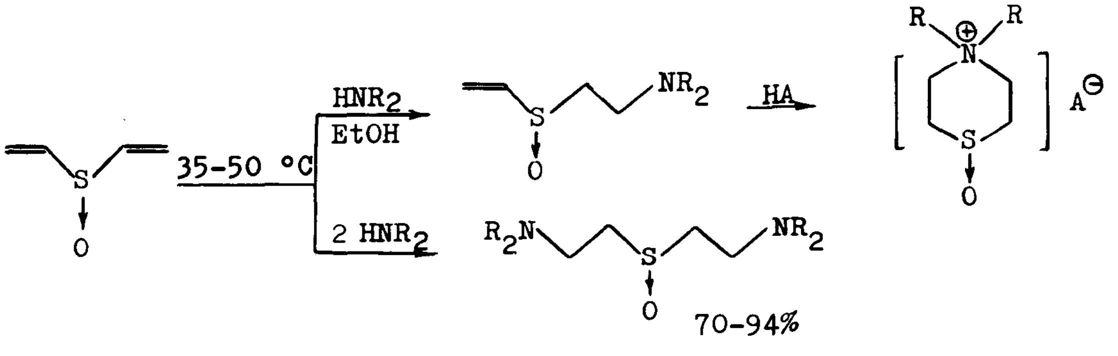
R = H (53%), organic radical (90–95%)



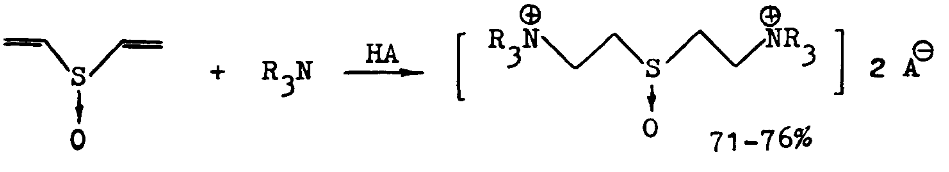
In this reaction there also are formed oligomers, in particular the 2:1 adduct of perhydrothiazine 1-oxide to divinyl sulfoxide.

One can easily direct the reaction of primary amines with divinyl sulfoxide to the formation of both *N*-substituted perhydrothiazine 1-oxides and open-chain 2:1 di-adducts. Here oligomerization has also been observed.

Secondary amines give mono- and diadducts. The former in the presence of acids are converted to quarternary salts of the corresponding perhydrothiazine 1-oxides.

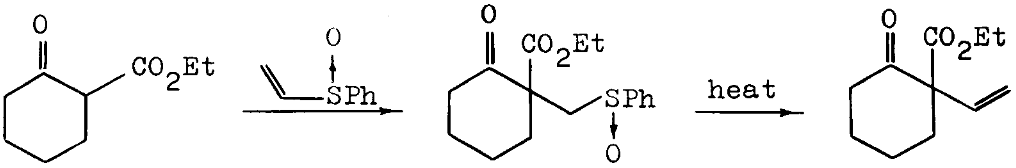


Likewise, quarternary mono- or diammonium salt formation takes place when tertiary amines and divinyl sulfoxide are allowed to interact in an acidic medium.

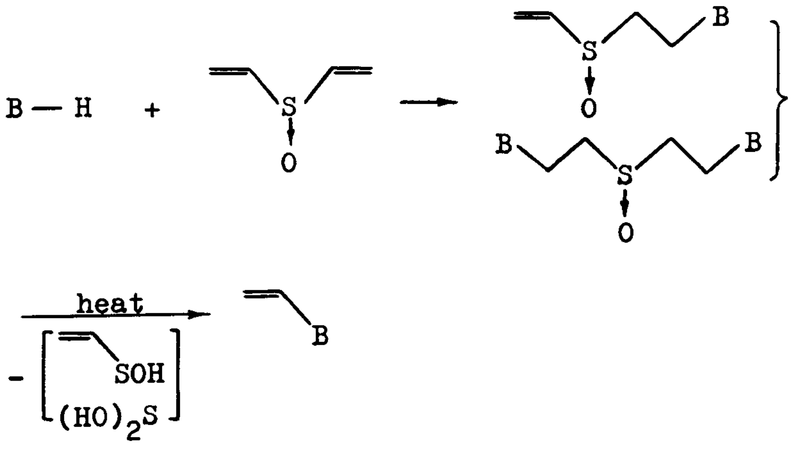


Smoothly proceeding polyadditions occur, as expected, between alkylenediamines and divinyl sulfoxide to yield poly-(aminoethyl sulfoxides) — a new type of multifunctional, highly polar polymers with numerous potential applications.

By analogy with the recently developed procedure for phenyl vinyl sulfoxide[65]



one can make use of divinyl sulfoxide as a twofold vinyl synthon to convert into vinylic derivatives not only various CH-acids, but alcohols and thiols as well.[66–68]



B = C—H active moiety, OR, SR

In conclusion: Novel simple acetylene based syntheses of unsaturated and cyclic chalcogenides including divinyl sulfide, divinyl sulfoxide, divinyl selenide, divinyl telluride, di(1,3-dibutadienyl)sulfide *S*-vinyl dithiocarbamate, thiophene, dihydrothiophene, selenophene, tellurophene and the like as well as their chemistry and applications are now in progress.

Acknowledgment: Since this paper presents mainly the results of our own school, thanks are due to the dedicated and skilled work of the following collaborators: S. V. Amosova, N. K. Gusarova, G. A. Kalabin, O. A. Tarasova, V. V. Kryuchkov, G. K. Musorin, G. M. Gavrilova, N. I. Ivanova, M. L. Alpert, V. A. Potapov and G. G. Efremova.

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