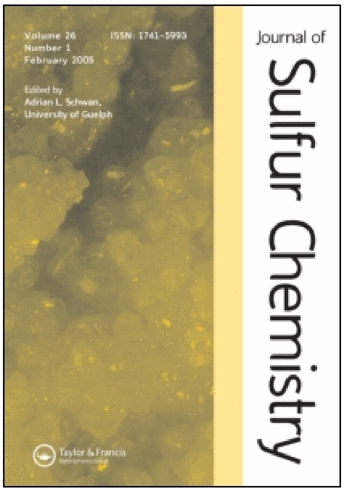

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Divinyl Sulfide: Synthesis, Properties, and Applications

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DIVINYL SULFIDE: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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The present review deals with the synthesis, reactions, structure, and physico-chemical properties of divinyl sulfide and its derivatives, new promising monomers, cross-linking agents, and intermediates for the synthesis of fine organic chemicals. Based upon extensive experimental data a new general approach to the activation of the addition of sulfur-containing anions to triple bonds using superbasic media and systems is presented for the first time in a self-consistent manner. New reactions of acetylene and substituted acetylenes with readily available sulfur compounds (hydrogen sulfide, alkali metal sulfides, hydrosulfides, di- and polysulfides, elemental sulfur, carbon disulfide, various thiono systems, esters and salts of thioacids) in superbasic media, leading to divinyl sulfide and derivatives thereof are discussed. The process for preparing divinyl sulfide from acetylene and hydrogen sulfide, which has been developed in the Soviet Union and has made this promising monomer one of the cheapest and most readily available chemical products is a central theme of this review. The polymerizaton of divinyl sulfide and the properties and application of its polymers and copolymers are considered. The subject matter of this review is presented in context with the chemistry of divinyl sulfide homologs and analogs.

CONTENTS

I. INTRODUCTION

Among the distinctive tendencies in modern organic chemistry the two following ones have been recognized recently. It is the vigorous development of the chemistry of organic sulfur compounds and the renewed interest in acetylene chemistry.

The development of organic sulfur chemistry is strongly stimulated by the vast potential resources (hundreds of millions of tons per year) of sulfur[1] isolated in the processing of petroleum, coal, natural gas, and sulfide ores.

Acetylene as one of the key chemical raw materials was considerably losing ground to petrochemical ethylene and propylene in the sixties, but has not lost, regardless of many predictions, its importance for major industrial organic syntheses. The increasing worldwide undersupply with petroleum raw materials[2] has already made many scientists and chemical engineers resort to acetylene.[3-7]

All this has created a strong impetus for a new independent approach at the interface between sulfur chemistry and acetylene chemistry which comprises design, development, and application of new monomers, chemicals, and biologically active compounds from cheap sulfur feedstock and acetylene for the manufacture of numerous products with new valuable properties.

A new approach to the activated addition of sulfur-containing anions across triple bonds involves the application of superbasic catalytic systems. The superbasicity is achieved by virtue of the ability of some heteroorganic compounds (dipolar aprotic solvents, macrocyclic polyethers and their analogs) to specifically solvate the cations of strong bases such as alkalis and alkoxides, thus increasing the reactivity of the conjugated anions as well as the ionization and polarization of acetylene molecules. Once introduced these catalytic systems have made possible whole families of new reactions of acetylene and its substitutes with readily available sulfur compounds: hydrogen sulfide, alkali metal sulfides and hydrosulfides, elemental sulfur, di- and polysulfides, carbon disulfide, various thiono systems, esters and salts of various thioacids. As a result, a series of efficient and industrially feasible methods for preparing divinyl sulfide, a promising cross-linking agent, bifunctional monomer and synthon for fine organic synthesis, have been developed.

Besides divinyl sulfide, the development of the above approach has made available for industrial application di(1,3-butadien-1-yl) sulfide, 2,5-dimethyl-4-methylene-1,3-oxathiolane, 2,4,5-trimethyl-1,3-oxathiolane, dihydrothiophene, divinyl selenide, divinyl telluride, divinyl sulfoxide, and other previously unknown or exotic, but potentially useful monomers and reagents.

The possibilities of this new approach are far from exhausted and the present work is not its epilog. It is rather the prolog of new work.

The present paper should not be considered as a complete reference list. Its limited volume has compelled the authors to omit the quotation of earlier work provided it is fully documented and commented in more recent papers, reviews, and monographs.

II. SYNTHESIS OF DIVINYL SULFIDE BY REACTION OF ACETYLENE WITH HYDRATED SULFIDES OF ALKALI METALS

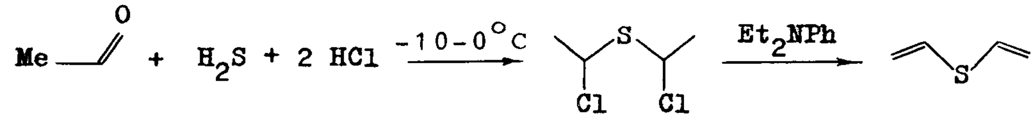
II.1. Earlier Methods of Divinyl Sulfide Preparation

Divinyl sulfide (DVS) was first synthesized by Helfrich and Reid in 1920.[8] When studying the reaction of 2, 2′-dichlorodiethyl sulfide with sodium ethoxide they isolated, instead of the expected 2,2′-diethoxydiethyl sulfide, DVS (the yield was not reported).

Later on, Bales and Nickelson,[9,10] while investigating the dehydrochlorination of 2,2'-dichlorodiethyl sulfide with alcoholic KOH, showed that the main product of this reaction also was DVS in yields from 26 to 35 % depending on the concentration of water in the reaction mixture. Davies and Oxford[11] reproduced the synthesis of DVS according to this technique. In this case, 2-chloroethyl vinyl sulfide was isolated and characterized as a side product. With excess KOH relative to 2,2'-dichloroethyl sulfide, 2-ethoxyethyl vinyl sulfide was isolated.

The interest in the synthesis of DVS from chloro substituted diethyl sulfides was renewed in the sixties. Thus, Schrader[12] was able to increase the yield of DVS to 47 % by changing the order of mixing, shortening the reaction time, and increasing the reaction temperature to 110 °C. It should be noted, however, that the reported boiling point 92–93 °C of the DVS obtained by the author is too high.

Brandsma and Arens[13] obtained DVS in 40 % yield by dehydrochlorination of 1,1'-dichlorodiethyl sulfide with *N*,*N*-diethylaniline at 100–150 °C.

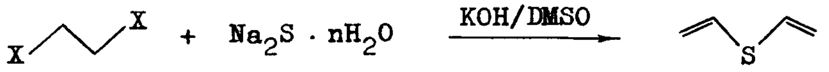


The dehydrobromination of 2,2'-dibromodiethyl sulfide with alcoholic KOH[14,15] also leads to DVS in a yield not exceeding 50 %.

The preparation of DVS by thiodiglycol dehydration is known. Doumani[16] used KOH as a dehydrating agent. The reaction is carried out by heating the reaction mixture to 190–220 °C during 20 minutes. Among the reaction products, DVS (the yield is not shown), its polymer, and 2-hydroxyethyl vinyl sulfide are observed. Georgieff and Dupré[17] studied this reaction in detail. It has been found that in this case a complicated mixture of DVS (36 %), 2-methyl-1,3-oxathiolane (9–10 %), 1,4-oxathiane (3.5 %), 2-hydroxyethyl vinyl sulfide (3.5 %), and some methyl vinyl sulfide is formed. The latter is likely to be formed by dehydration of 2-hydroxyethyl methyl sulfide present in the thiodiglycol as an impurity.

An attempt to use anhydrous potassium hydrogen sulfate as a dehydrating agent did not lead to DVS, 1,4-oxathiane being obtained as the reaction product.[18]

The reaction of hydrated sodium sulfide with dihaloethanes in a KOH-DMSO medium recently afforded DVS in 35 % yield.[19]



X = Cl,Br; n = 4,9

Vinyl halides react also with hydrated sodium sulfide under the above conditions, the yield of DVS being considerably higher (73–87 %), based on the vinyl halide consumed, the conversion of which is about 50 %.[20]

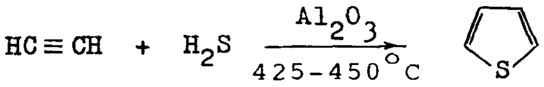
In 1939 a paper[21] concerning microimpurities contained in acetylene produced by the carbide method was published. About 95 % of the sulfur-containing products isolated from acetylene at low temperature proved to be DVS.

The DVS content depends on the temperature of the carbide quenching and ranges from 100–270 mg/m^3 (wet generator, 100 °C) to 1000–2700 mg/m^3 (dry generator, 60–70 °C).[22] The appearance of DVS in acetylene may be due to the presence of traces of calcium sulfide in commercial calcium carbide.[23,24]

A method for preparing DVS based on the decomposition of calcium carbide-sulfur alloys with water vapor was claimed in a patent.[25] The yield of DVS is shown in the most reliable example of this patent to be as low as 26 %, being achieved by a complicated, multi-step, and energy-consuming method: melting of the components at 1600 °C, decomposition of the reaction mixture, use of a vapor-gas current, handling of large volumes of a semisolid mass which is difficult to stir. As emphasized in this patent the decomposition should be carried out under special, strictly controlled conditions providing immediate removal of DVS from the reaction zone. When these conditions are not fulfilled, for example with excess water, not even traces of DVS are formed. Nothing was reported concerning the purity and physical properties of the DVS obtained. Moreover, the decomposition of the carbide-sulfur alloy with water may lead to the formation of other sulfur compounds, in particular those from hydrogen sulfide and acetylene (for example thiophene[26] and ethyl vinyl sulfide[27] rather similar to DVS in their properties, and a number of other organic sulfur compounds as well).

There is evidence that DVS is present in a number of plants. Thus, as early as 1887 Semmler,[28] from chemical properties and elemental analysis of the extract of one of the wild-growing garlic species (*Allium ursinum* L.) identified DVS as a component of the mixture analyzed. Although the DVS properties reported by this author (b.p. 101 °C, d_4^{20} 0.9125) differ much from the true values this may be due to the presence of impurities in the sample. The year of 1952 provided new evidence[29] for the presence of DVS in garlic (in this case *Allium sativum*). Besides DVS its oligomer containing five sulfur atoms was also isolated. In the author's opinion,[29] it is the presence of polyvinyl sulfide components that accounts for the bactericidal activity of these natural products.

There are known some unsuccessful attempts to synthesize DVS by reaction of acetylene with hydrogen sulfide or its salts. As early as 1915 Chichibabin[30,31] showed that the high-temperature reaction of acetylene with hydrogen sulfide on alumina led to thiophene the content of which in the catalysate can be as high as 40 %.

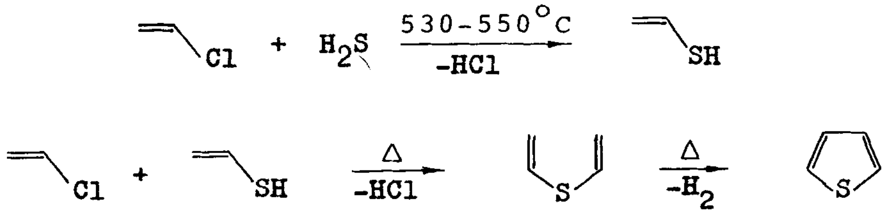


Alkylthiophenes, ethanethiol and other higher mercaptans were also observed in the catalysate as side-products.

Using sulfides of Pb, Mn, Cr, Mo, Co, Ni on the bed at a temperature of 650–750 °C as the catalysts of the above reaction the thiophene content of the catalysate could be increased to 60 %. Carbon disulfide and alkylthiophenes were also found among the reaction products.[32,33] Analogous results were obtained by Broun[34,35] and Arnold.[36]

There is known an account of work[37] on the synthesis of thiophene in 50 % yield from hydrogen sulfide and acetylene or acetylene-containing gases in the γ-alumina bed electrocracking of liquid petroleum products.

DVS is believed to be an intermediate in the high-temperature synthesis of ethenethiol and thiophene from vinyl chloride and hydrogen sulfide.[38]

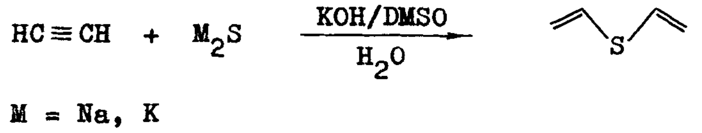


The yields of ethenethiol and thiophene are 67 and 24 %, respectively, based on the vinyl chloride consumed, the degree of conversion being 50 %.

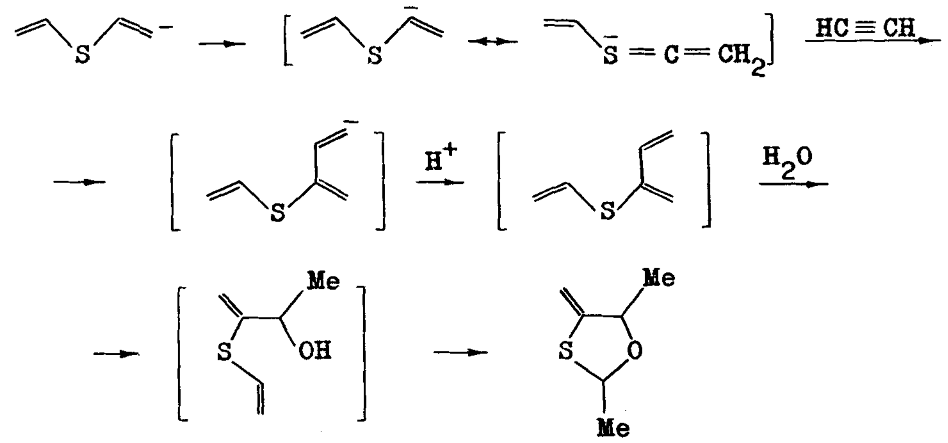
Reppe[27,39] attempted to vinylate hydrogen sulfide in the presence of alkali and alkaline earth metal hydrosulfides in water and ethylene glycol. Instead of the expected DVS he obtained a complicated mixture of trimeric thioacetaldehyde, ethanethiol, ethyl vinyl sulfide, 1,2-di(ethylthio)ethane and 1,2-ethanedithiol. In none of the cases described DVS was found even in traces.

II.2. Reaction of Acetylene with Sulfide Ion under Pressure

The first reaction of acetylene with sulfide ion to give DVS was carried out in DMSO in an autoclave at a temperature of 100–110 °C under pressure. With sodium sulfide as the source of sulfide ion the yield of DVS was 60 % and 82 % in the case of potassium sulfide.[40–42] The optimal yield (98 %) was achieved when a 4-fold molar excess of KOH and a 10-fold molar excess of DMSO relative to $Na_2S{\cdot}4H_2O$ were used.[43]



Alongside, 2,5-dimethyl-4-methylene-1,3-oxathiolane **1** was formed in 15 % yield.[44] One of the possible routes to the above product is the isomerization of the DVS carbanion followed by its addition to acetylene and subsequent protonation and hydration.



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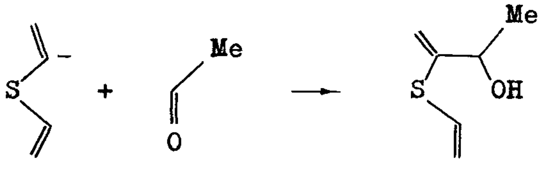
The same precursor of the oxathiolane can also be formed by reaction of the isomerized divinyl sulfide carbanion with acetaldehyde, the product of acetylene hydration. *cis*-1-Vinylthio-1-buten-3-ol has been identified[45,46] as a product of the reaction of elemental sulfur with acetylene in aqueous-alkaline solution in the presence of tin chloride. The selenium [45,47] and tellurium[45,48] analogs of this precursor have been isolated recently from the products of the reaction between selenium (tellurium) and acetylene under almost the same conditions.



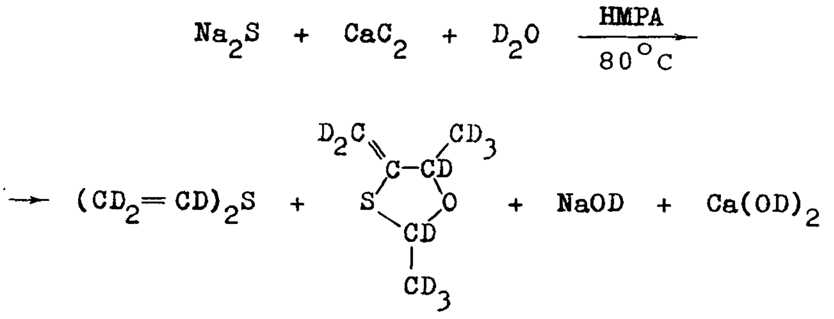
The solvent is of primary importance in this reaction.[43] Thus, the yield of DVS in DMSO is 79 % (not optimized). If hexamethylphosphoramide (HMPA) or sulfolane are used under analogous conditions, the yield of DVS is much lower (43 and 18 %, respectively), the reaction being accompanied by partial decomposition of the solvents. In water, diethyleneglycol divinyl ether, 2-methyl-1,3-dioxolane, dimethylformamide, dioxane, and tetrahydrofuran, DVS is formed under the same conditions in yields as low as 1–5 %.

At higher temperature (140–150 °C) the content of the DMSO cleavage products (methyl vinyl sulfide, dimethyl sulfide) increases sharply in the reaction mixture as well as that of benzene, toluene, 2-vinyloxy-1,3-butadiene,[49] and *cis*-vinyl 1-propenyl ether[50] which are the products of the cyclooligomerization and hydration of acetylene.

The proton donor in the synthesis of DVS from sodium sulfide with acetylene is water. An increase in the water concentration (the degree of soldium sulfide hydration) facilitates the homogenization of the reaction mixture. At higher water concentrations (starting with an amount corresponding to the tetrahydrate $Na_2S{\cdot}4H_2O$) a decrease in the yield of DVS and an increase in the yield of oxathiolane **1** are observed.[43]

In 1.5-2-fold excess H_2O with respect to the theoretically required quantity it is possible to inhibit the formation of oxathiolane **1** completely and to obtain DVS with a purity of 99–99.5 % in 98 % yield.

A preparative method for the synthesis of perdeuterated DVS and oxathiolane **1** has been developed.[51] DMSO-H_6 is not the appropriate solvent for preparing the deuterated products since it is prone to proton exchange under alkaline conditions.[52] Based on data[53] showing the absence of proton exchange between CH_3-tritium-labeled toluene and HMPA the latter have been used[51] as the solvent although, as stated above, in this case the yield of DVS is lower than in DMSO. The source of deuterium was deuterium oxide (D_2O) and the source of deuterated acetylene was calcium carbide which reacts with heavy water in the course of the reaction. Under these conditions calcium carbide is known[54] to be a suitable starting material for preparing vinyl ethers. Consequently, this particular reaction of CaC_2 and Na_2S in the presence of D_2O in HMPA affords DVS-D_6 and 2,5-dimethyl-4-methylene-1,3-oxathiolane-D_{10} in 34 and 9 % yield, respectively.



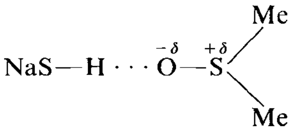
The reaction proceeds in the presence of a two-fold excess of CaC_2. Due to a considerably lower acidity of water in dipolar aprotic solvents,[55] CaC_2 reacts with D_2O more slowly than usually. This requires extra quantities of water (up to one third more than under optimal conditions).[43]

II.2.1. Some features of the Na_2S—H_2O—DMSO system The dissolution of sodium sulfide in aqueous DMSO (with an H_2O content of less than 40 %) is a process of selective NaSH extraction, the greater part of the NaOH remaining in the precipitate:[56]

$$Na_2S + H_2O \rightleftarrows NaSH + NaOH$$

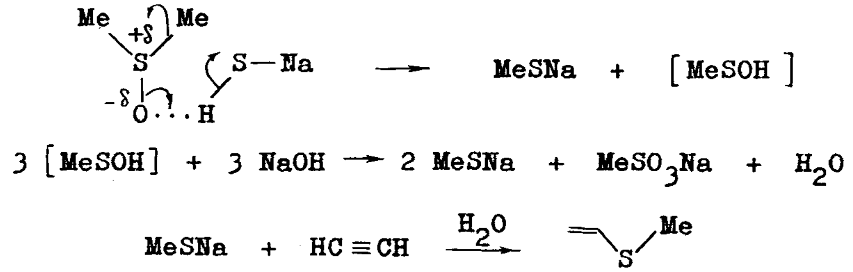
At low H_2O content practically only NaSH is present in the liquid phase. The IR spectrum of Na_2S dissolved in DMSO displays an absorption band at 2570 cm^{-1} corresponding to the S-H stretch.

This indicates the existence of a strong specific interaction between sodium hydrosulfide ion pairs and DMSO. This seems to be the H-bonding of the SH group to the S=O group (the latter is known to be a strong proton acceptor):[53]



$$NaS{-}H\cdots\overset{-\delta}{O}{-}\overset{+\delta}{S}(Me)_2$$

These complexes may be responsible, for example, for the concomitant formation of methyl vinyl sulfide always present to some degree as one of the products of the reaction of $Na_2S{\cdot}nH_2O$ with acetylene in DMSO:



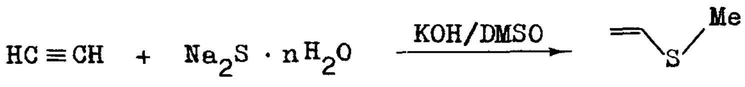
In the above solvate, NaSH·DMSO is essentially equivalent to the separated ion pair $Na^{+-}SH$, and thus the nucleophilicity of the hydrosulfide ion should be strongly enhanced. It is this fact that may lie in the specific activating effect of DMSO on the nucleophilic addition of sulfide ions to triple bonds.[56]

II.2.2. Optimization of the DVS synthesis and evaluation of the main and side reaction rates The application of an experimental design to the study of the synthesis of DVS has resulted in the determination of high-yield procedures and conditions for obtaining the main product in yields up to 90 %.[57–59]

In the search for optimal conditions for the process a step-by-step method to study the response surface was used. This allowed one to find, without using high-order polynomes for the description of the experimental data, the extremum of the function optimization parameter dependent, in an unknown way, on many arguments and then to study this dependence. If necessary, a steep ascend along the response surface was performed (by the Box-Wilson method).[59]

As stated above, in addition to the main reaction course the system studied involves some side processes. These are:

1. Formation of methyl vinyl sulfide



2. Heterocyclization of acetylene with sulfide ions and water to 2,5-dimethyl-4-methylene-1,3-oxathiolane **1**

$$HC{\equiv}CH + Na_2S{\cdot}nH_2O \xrightarrow[DMSO]{KOH} \mathbf{1}$$

The actual mechanism and intermediate stages of these reactions are still unknown.

The investigation of the reaction under laboratory conditions helped to determine the effect of reaction time (x_1, h), temperature (x_2, °C), quantity of alkaline (KOH) reagent (x_3, %), and acetylene pressure (x_4, atm) on the yield of DVS (Table I). The concentration of sodium sulfide was constant and in excess in all runs.

The yield of DVS was taken as the optimization parameter. The half-replica of the plan 2^4 was chosen as the first plan. In realization of this plan fairly high yields of DVS were achieved (Table I, runs 4 and 5) and "mild" reaction conditions which provide good results at rather low acetylene pressure were found (Table I, runs 1 and 8). It was necessary to determine in which way the reaction conditions should be changed in order to increase the yield of DVS and to keep it high while going to atmospheric pressure of acetylene. For this purpose we constructed a mathematical model adequately describing the experimental data.

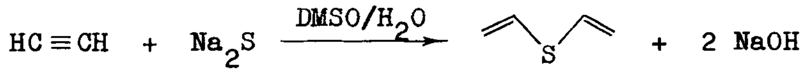
The analysis of the model shows that large yields of DVS at high pressures (about 10 atm) require use of alkali (KOH), the reaction time being about 1 hour, whereas at an acetylene pressure close to atmospheric (1.5 atm) the same high yields can be obtained without addition of KOH, but in this case the reaction is more time-consuming.

TABLE I

Planning Matrix and Results of Optimization of the Synthesis of DVS at Higher Acetylene Pressure

Run no.	x_1	x_2	x_3	x_4	y
1	1.5	110	0	4	82 ± 4
2	0.5	90	0	4	34 ± 4
3	1.5	90	0	10	75 ± 2
4	0.5	110	0	10	90 ± 2
5	1.5	90	1.25	10	90 ± 3
6	0.5	110	1.25	10	55 ± 3
7	1.5	110	1.25	4	54 ± 3
8	0.5	90	1.25	4	78 ± 2

It is necessary to study the effect of the alkaline additive due to the accumulation of alkali in the course of the reaction.



In this case the elucidation of the effect of alkaline additive sheds some additional light on the reaction mechanism. The research performed has made it possible to go over to the synthesis of DVS on bench and pilot plant apparatus of volume up to 400 l at acetylene pressure from 1.5 atm to atmospheric.[58]

Further study of the synthesis of DVS was carried out at constant acetylene pressure (1.5 atm) and constant temperature (95 °C). The effect of the reaction time, the amount of reagents, the molar ratio of the alkaline additive and sodium sulfide on the yield of DVS was examined. Two types of alkaline additives (NaOH and KOH) have been tested. The results obtained have confirmed the conclusion drawn earlier that the reaction can be carried out with high yields of DVS without special alkaline additives. The best yield achieved is 91 % of DVS (96 % purity), reaction time 8 hours.[57]

The results of these tests have been used to design a more precise model of the process and to derive some tentative kinetic parameters.[58] If this model adequately describes the formation of the main product depending on the starting conditions and the reaction time, the rate of the formation of the product at a given time can be calculated by the differential method. The resulting rate values can be applied in the estimation of kinetic parameters (by the least-square method) from the Arrhenius equation. The yields of DVS and by-products (methyl vinyl sulfide and oxathiolane **1**) are listed in Table II.

The least-square method for DVS and methyl vinyl sulfide gave a regression equation describing not only the experimental data, but also the boundary conditions (no product at the start of the reaction) as well. The equation describing the formation of DVS is as follows:

$$y_1 \cdot 10^2 = (103.7 \pm 3.9) + (40.1 \pm 1.6)\, x_1 + (3.8 \pm 1.7)\, x_2 - (19.7 \pm 4.5)\, x_2^2$$

$$S_0 = 4.83, \quad f = 6$$

The hypothesis concerning the adequacy of the above equation is not rejected by the Fisher criterion.

The above equation has no x_1x_2 term denoting the concentration—time interaction. Furthermore, this term, when introduced into the equation, deteriorates considerably the correlation coefficient and the standard error, which suggests that the reaction rate does not depend on the reagent concentration x_2 (sodium sulfide).

Finally, for the formation of DVS a zero reaction order with respect to sodium sulfide and a tentative reaction rate constant at 95 °C were obtained:

$$k = (1.68 \pm 0.06) \cdot 10^{-3}\ (\text{mole/l} \cdot \text{min})$$

The results obtained give good reason to believe that the reaction proceeds both in the kinetic region and as a homogenous process due to the sulfide ions present in the DMSO solution. Owing to the limited solubility of Na_2S in DMSO the concentration of these anions remains approximately constant during the reaction and this accounts for the zero order in sodium sulfide.

The same zero order with respect to sodium sulfide was found for the formation of methyl vinyl sulfide, the rate constant at the same temperature being:

$$k = (10.5 \pm 2.5) \cdot 10^{-5}\ (\text{mole/l} \cdot \text{min})$$

Since methyl vinyl sulfide is formed from DMSO which has nearly constant concentration during the reaction, the pseudo-zero order is also quite understandable in this

TABLE II

Synthesis of DVS without Alkaline Additive at an Acetylene Pressure of 1.5 atm. Experimental Conditions and Results

Run No.	x_1, h	x_2, mole[a], Na_2S	DVS, $y_1 \cdot 10^2$, mole/l	Methyl Vinyl Sulfide $y_2 \cdot 10^2$, mole/l	1 $y_3 \cdot 10^2$, mole/l
1	4	30	55.49	3.39	5.39
2	8.5	15	84.81	2.86	0.53
3	12	30	128.92	6.34	1.02
4	7	15	70.06	4.49	1.15
5	10	30	105.39	8.26	5.10
6	9	20	108.43	16.97	—
7	7	30	84.04	—	—
8	6	20	81.95	—	—

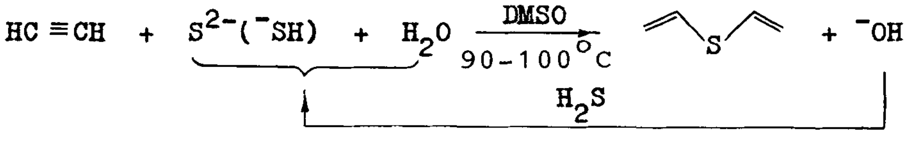
[a] The DMSO volume is 17.6 l

reaction, assuming constant concentrations of acetylene and Na_2S. These results support the conclusion concerning the order of the main reaction with respect to sodium sulfide.

The polynomial model describing the formation of the second side-product **1** does not include the boundary conditions. The calculations show the induction period for this reaction to be 1.0–1.5 hours. The concentration of the oxathiolane **1** reaches its maximum after 6–7 hours and then decreases. This means that the oxathiolane **1** is not sufficiently stable under the reaction conditions and undergoes further conversion.

It should be noted, however, that the optimization[60] is not complete. The reaction rates and selectivity of the process in a reactor with a stirrer are greatly affected by the intensity of the stirring. Thus, when the rotation velocity of the anchor stirrer is 100 revolutions per minute (25-l reactor) the yield of DVS is not high (~40 %) and the selectivity of the process is poor. However, at a rotation velocity of the turbine stirrer of 360 revolutions per minute (40-l reactor) commercially acceptable results were obtained (yield of DVS 86.7 %, purity 96.4 %).[60]

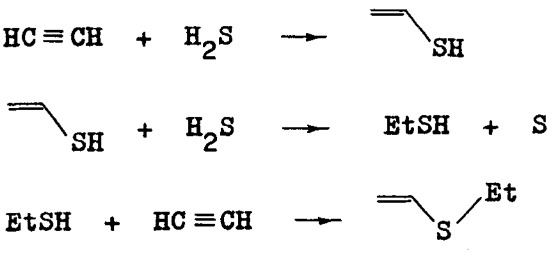
II.2.3. Reaction of acetylene with hydrogen sulfide in the alkali-DMSO system The reaction of acetylene with sodium sulfide is essentially a nucleophilic addition of the sulfide ion to the triple bond. The sulfide ions can be generated from hydrogen sulfide and alkali and this gives rise to a continuous production of DVS directly from hydrogen sulfide and acetylene.



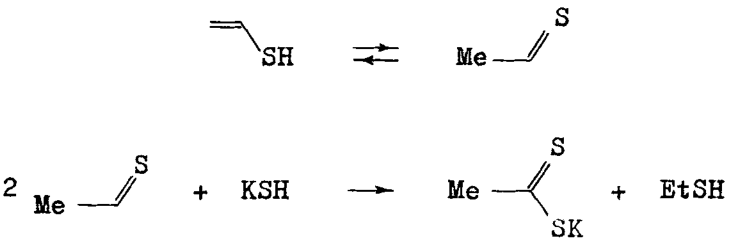
This reaction was carried out[40–42] at atmospheric pressure and with simultaneous feeding of acetylene and hydrogen sulfide to an aqueous dimethyl sulfoxide solution containing KOH. The side-products of the reaction are ethyl vinyl sulfide, ethanethiol, and products formed from DMSO, such as dimethyl sulfide and methyl vinyl sulfide.

The effect of the hydrogen sulfide/acetylene feed rate on the yield and ratio of the reaction products has been studied.[61] The most suitable ratio of the volumetric rates of hydrogen sulfide and acetylene supply is 1 : 3.

The ethanethiol and ethyl vinyl sulfide found in the condensate seem to be formed because of the transformation of all alkali to hydrosulfide in the reaction mixture. In the presence of the above salt the reaction of hydrogen sulfide with acetylene can proceed according to the following scheme:[62,63]



An alternative formation of ethanethiol may involve oxidation-reduction transformations of the intermediate thioacetaldehyde:



These conversions (a peculiar "organosulfur" analog of the Tishchenko reaction[64]) should lead to the accumulation of dithioacetic acid salts in the reaction medium and, finally (as a result of interaction with alkali) to acetates.

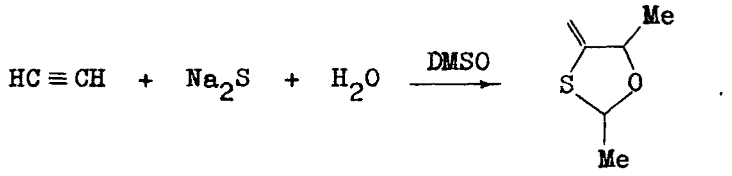
An unexpected result was obtained[61,65] when the reaction was carried out in HMPA. Under these conditions, practically pure ethanethiol[65] with a small content (up to 2 %) of ethyl vinyl sulfide are removed with the gas flow from the reaction mixture. Thus, a method for preparing ethanethiol from acetylene and hydrogen sulfide in yields up to 70 % (based on the acetylene consumed) has been developed.[65] The trapping of ethanethiol is observed only after complete conversion of the alkali to alkali metal hydrosulfide as proven by potentiometric titration of the reaction mixture. In this case the above scheme[62] is likely to be operative. Unlike DMSO, HMPA is a solvent which efficiently solvates and, consequently, stabilizes free electrons.[53] This may explain the specific accelerating effect of this solvent on oxidation-reduction processes. In DMSO the reduction of ethanethiol ought to be inhibited since the solvent behaves as an oxidant of the thiol function,[66] thus causing the formation of dimethyl sulfide.

The synthesis of DVS by reaction of acetylene and hydrogen sulfide at atmospheric pressure has been performed in a 5-l bench apparatus. The possibility of preparing DVS from acetylene and hydrogen sulfide has been demonstrated[40–42] and the route to continuous production of DVS by this reaction has been outlined.

The advantage of this process consists also in the utilization of hydrogen sulfide, a waste product from oil and gas processing, metallurgical, chemical, and pulp and paper industries.

II.2.4. Other reactions of acetylene with hydrated sodium sulfide

II.2.4.1. 2,5-Dimethyl-4-methylene-1,3-oxathiolane As stated above, the reaction of acetylene with sodium sulfide in an aqueous dimethyl sulfoxide medium affords, along with DVS, an unsaturated heterocycle, 2,5-dimethyl-4-methylene-1,3-oxathiolane **1** in 24 % yield.[44]



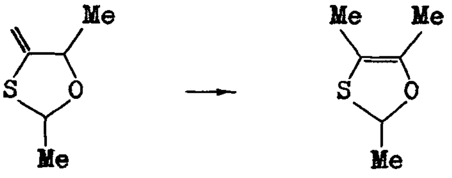
1

cis : trans ≃ 1 : 1

The yield of the heterocycle **1** depends on the ratio of sodium sulfide, alkali, water, and DMSO and is also determined by the cations present in the reaction mixture. The least favorable for this reaction are potassium cations. Use of barium hydroxide as the catalyst can lead to the oxathiolane **1** in 29 % yield.[43,67] Cuprous chloride is an even more efficient additive which increases the **1** content of the reaction products to as much as 60 %.

According to ^1H and ^{13}C NMR data **1** is a mixture of *cis*- and *trans*-isomers.[68] The structure of **1** was also confirmed by IR and mass spectroscopy.[68]

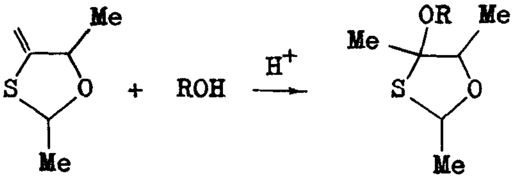
Some independent data on the structure of **1** have been obtained by studying its isomerization to 2,4,5-trimethyl-1,3-oxathiole **2**.[68]



1 2

The isomerization was carried out directly in an NMR spectrometer tube. In 10 % CCl_4 solution at 100 °C during 90 min, 70 % of **1** isomerizes to the oxathiole **2**.[68] Under the same conditions, in the presence of benzoyl peroxide, only 35 % of **1** undergoes isomerization. Atmospheric oxygen initiates this isomerization, though slowly, whereas **1** sealed in an ampoule under nitrogen does not isomerize at all.

The adducts of methanol **3**[68] and ethanol **4** to the oxathiolane have been obtained.

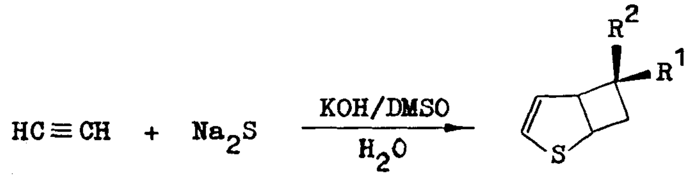


3 R = Me

4 R = Et

A mixture of four methoxy-oxathiolane **3** isomers has been studied in detail by means of ^1H NMR spectroscopy.[68]

II.2.4.2. 2-Thiabicyclo[3.2.0]-3-heptenes Varying the conditions of the reaction of acetylene with sodium sulfide,[40–42,44] besides formation of DVS and **1**[43] in the above system one can recognize another heterocyclization leading to 2-thiabicyclo[3.2.0]-3-heptenes **5–7**.[69]



5-7

$R^1 = R^2 = H$ (**5**); $R^1 = H$, $R^2 = Me$ (**6**); $R^1 = Me$, $R^2 = H$ (**7**)

Three individual compounds, **5**–**7**, have been isolated from the reaction mixture by GLC in about 3 % yield.[69]

From ^{1}H NMR, IR spectra, elemental analysis, and mass spectrometry data, the product with the lowest boiling point is 2-thiabicyclo[3.2.0]-3-heptene **5**, the two other products being its 6-methyl substituted *exo*-**6** and *endo*-forms **7**.[70] Ten alternative structures have also been considered and ruled out by NMR spectroscopy.[70]

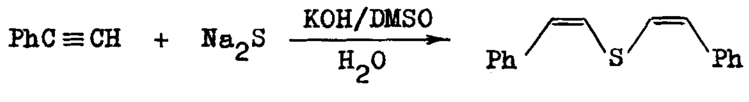
The above one-step synthetic route[69] to a new unusual bridged heterocyclic system such as 2-thiabicyclo[3.2.0]-3-heptene may be used, in spite of its low yield, as a preparative method due to its remarkable simplicity and availability of the starting materials as well as the lack of other known approaches to such a system.

III. SYNTHESIS OF SUBSTITUTED DIVINYL SULFIDES AND THEIR CYCLIC DERIVATIVES FROM SUBSTITUTED ACETYLENES

The reaction of substituted acetylenes with hydrated sodium sulfide opens new possibilities for the synthesis of divinyl sulfides with various substituents.

III.1. Synthesis of Bis(2-phenylvinyl) Sulfide

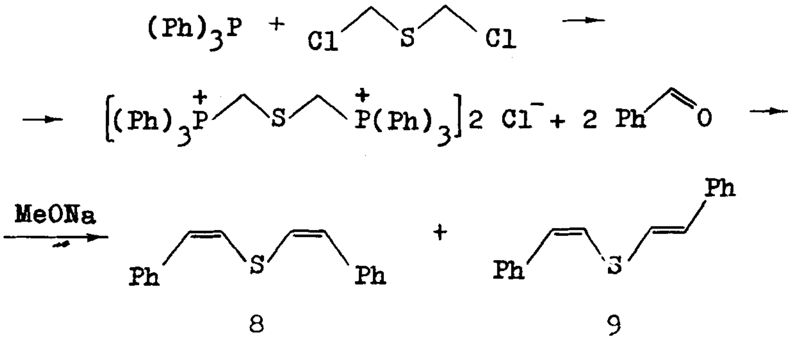
Phenylacetylene readily reacts with hydrated sodium sulfide in a DMSO medium in the presence of potassium hydroxide at 100 °C.[71,72]



8

According to the rule of *trans*-nucleophilic addition of thioanions[73] to monosubstituted acetylene the above reaction gives bis(2-phenylvinyl) sulfide of *cis,cis*-configuration **8** in 67 % yield, the latter readily transforming further into the *cis,trans*-isomer **9**. In the presence of hydroquinone the yield is 91 %. This reaction may be carried out successfully at a lower temperature (20 °C).

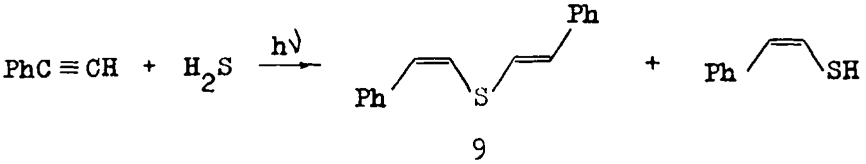
A two-step method for preparing a mixture of the *cis,trans*- and *trans,trans*-isomers of bis(2-phenylvinyl) sulfide by the Wittig reaction in 27 % yield (based on the starting triphenylphosphine) is known.[74]



8 9

However, the authors[74] statement that in this case they could isolate *trans,trans*-bis(2-phenylvinyl) sulfide (m.p. 42–43 °C) does not seem to be true. No ^1H NMR spectra are presented.[74] The melting point of the sample coincides with that of *cis,cis*-**8**.[72]

The X-ray initiated addition of hydrogen sulfide to phenylacetylene affords *cis,trans*-bis(2-phenylvinyl) sulfide **9** and 2-phenylethenethiol.[75]

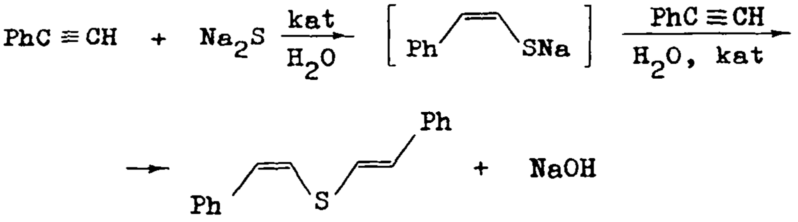


9

The configuration of the compounds obtained has not been reported.[75] According to the melting point, however, the product corresponds to *cis,trans*-bis(2-phenylvinyl) sulfide **9**. Other acetylenes (acetylene, propyne, 3,3,3-trifluoropropyne, 2-butyne, 1,1,1,4,4,4-hexafluoro-2-butyne) form neither DVS nor its substitutes under analogous conditions.[75]

The photochemical addition of hydrogen sulfide to phenylacetylene gives bis(2-phenylvinyl) sulfide (a mixture of three isomers) in 41 % yield.[76]

To accelerate the nucleophilic addition to acetylene, the KOH-triethylphosphine oxide (TEPO) system has also been recommended.[77] In this case the reaction of hydrated sodium sulfide with phenylacetylene leads to **8** in 90 % yield. When carried out in biphasic catalytic systems, the reactions of nucleophilic substitution often display preparative advantages and become widely used in organic synthesis.[78–80] However, before our investigations[81] it was still uncertain whether the anions generated in this system are of higher reactivity in nucleophilic addition to the triple bond as well. Crown ethers and tetraalkylammonium salts appeared to catalyze efficiently the reaction of phenylacetylene with sodium sulfide in the two-phase system aqueous Na_2S–phenylacetylene.



When dibenzo-18-crown-6 is used as a catalyst the sulfide **9** is formed in 39 % yield (based on consumed phenylacetylene; degree of conversion 22 %).[81]

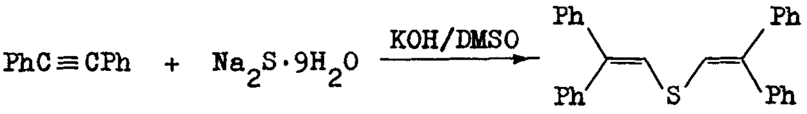
The reaction of sodium sulfide with phenylacetylene under phase-transfer conditions with triethylbenzylammonium chloride as catalyst gives the sulfide **8** in 22 % yield (based on consumed phenylacetylene; 29 % conversion). Without catalyst **8** is formed under the same conditions in 11 % yield with 16 % phenylacetylene conversion.[81]

The kinetics of the reaction of phenylacetylene with sulfide ions have been studied[82,83] in a medium of aprotic dipolar solvents: HMPA, DMSO, TEPO. The main kinetic parameters of the process, *i.e.*, the rate constants of **8** formation in all three solvents and, besides, the enthalpy ($H^{\neq}_{328} = 7.3$ kcal/mol and entropy $S^{\neq}_{328} = -46$ e.u.) of activation in HMPA have been determined.[82]

The reaction rate depends on the medium and decreases in the following order: HMPA > DMSO > TEPO.

III.2. Synthesis of Bis(2,2-diphenylvinyl) Sulfide and Tetraphenylthiophene

Diphenylacetylene reacts with hydrated sodium sulfide in DMSO in the presence of alkali to form an anomalous product, bis(2,2-diphenylvinyl) sulfide **10**, in 20 % yield instead of the expected bis(1,2-diphenylvinyl) sulfide.



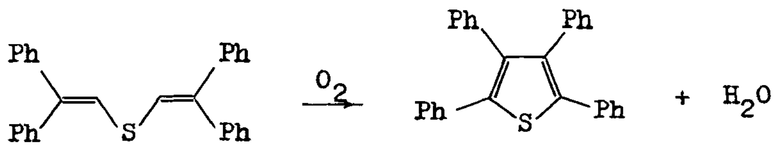
10

The structure of **10** has been proven by spectral methods, dipole moment measurements and chemical conversion,[84] including ozonization.

1,2-Migration of the phenyl group is known to occur upon heating metal derivatives (Mg, Li, K, Na) of 1,1,1-triphenylethane, 2,2-diphenylpropane, and 1,1-diphenyl-1-*p*-tolylethane (the Grovenstein-Zimmermann rearrangement[85–89]) as well as during the conversion of diarylhaloethylenes to diarylacetylenes under the action of strong alkali such as sodium ethoxide, potassium *t*-butoxide, sodium or potassium amide in liquid ammonia, and lithium alkyls (the Fritsch-Buttenberg-Wiechell rearrangement[89–93]).

Treatment of **10** with KOH in wet DMSO leads to a reverse 1,2-migration of a phenyl group as evidenced by the isolation of diphenylacetylene in 49 % yield.[94] This migration is also observed in the hydrolysis of **10** in the presence of $TiCl_4$,[95] phenyl benzyl ketone being formed in this case. An alternative scheme for the formation of this compound, *i.e.* hydration of diphenylacetylene under the same reaction conditions could not be confirmed experimentally.[94]

The reverse 1,2-migration of the phenyl group also occurs in the formation of tetraphenylthiophene from **10** upon heating in air at 200–220 °C. Under these conditions bis(2,2-diphenyl) sulfide is almost quantitatively oxidized by atmospheric oxygen to tetraphenylthiophene:[84]

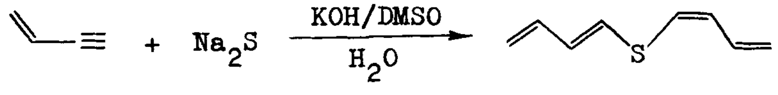


The structure of tetraphenylthiophene has been confirmed[96] by ^1H NMR, IR, UV, mass spectroscopy, and thin layer chromatography. According to all these characteristics, the tetraphenylthiophene synthesized does not differ from an authentic sample obtained by[97] and chromatographically purified.

III.3. Synthesis of Di(1,3-butadienyl-1) Sulfide, Dihydrothiophene and 1-Vinyl-2-thiabicyclo [3.2.0]-3-heptene

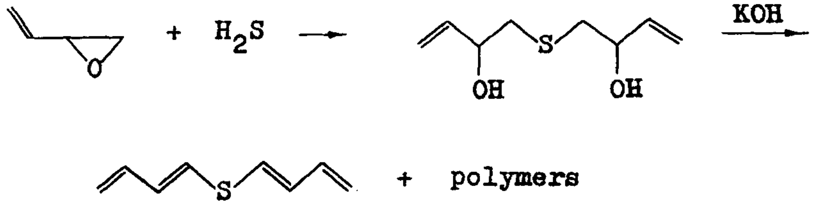
Until recently the absence of information on the reactions of vinylacetylenes with hydrogen sulfide seemed quite surprizing on the background of much work concerning the addition of organylthio anions to the triple bond.

Investigations[98,99] have indicated that the reaction of vinylacetylene with $Na_2S{\cdot}9H_2O$ in the KOH-DMSO system at 70–110 °C leads to di(1,3-butadienyl-1) sulfide **11** in 91 % yield (based on $Na_2S{\cdot}9H_2O$ consumed) under optimal conditions.

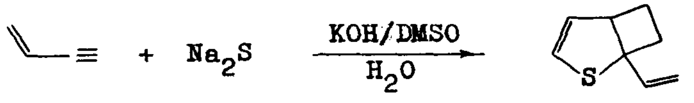


11

Di(1,3-butadienyl-1) sulfide has been prepared previously in 50 % yield by reaction of butadiene monoxide with hydrogen sulfide followed by dehydration of the intermediate formed in the presence of KOH at 250 °C.[16] However, neither physical nor structural data for the di(1,3-butadienyl-1) sulfide synthesized in this way have been reported.



Since the reaction of acetylene with sodium sulfide affords 2-thiabicyclo[3.2.0]-3-heptene, the corresponding bicycle might be expected in the case of vinylacetylene, too. In fact, 1-vinyl-2-thiabicyclo[3.2.0]-3-heptene **12** has been isolated and identified[100,101] in yields reaching 26 % in the best runs.



12

Shown to be fairly general, this reaction presents a route to new heterobicyclic compounds of rather uncommon structure.

The presence of noticeable amounts of 2,5-dihydrothiophene **13** (approximately 20 % of the quantity of compounds **11** and **12**) in the reaction mixture does not seem unexpected.

13

The conditions in which the above reaction dominates and gives a nearly quantitative yield of 2,5-dihydrothiophene have been found.[102] This is achieved by resorting to the HS^- anion (from NaSH).

The structure of **11** and **12** have been established by ^1H and ^{13}C NMR spectroscopy[100,103,104] and confirmed by IR and mass spectra.[105]

The preparative conditions for the reaction of vinylacetylene with sodium hydrosulfide which allow 2,5-dihydrothiophene to be obtained in 97.8 % yield (based on consumed sodium hydrosulfide at 40–50 % conversion) have been reported.[102,106] Thus, 2,5-dihydrothiophene has become a readily available compound with potential for wide application.

An important role in this reaction is played by the superbasic system MOH—DMSO (M = Na, K) which not only increases the reactivity of the anions, but also activates the triple bond by specific solvation of the acetylenes which imparts additional polarization to the latter as evidenced by the high solubility of acetylene[107] in DMSO and HMPA, strong solvation of phenylacetylene in these solvents,[108,109] and chemical reactions of DMSO with acetylenes.[40,110–112]

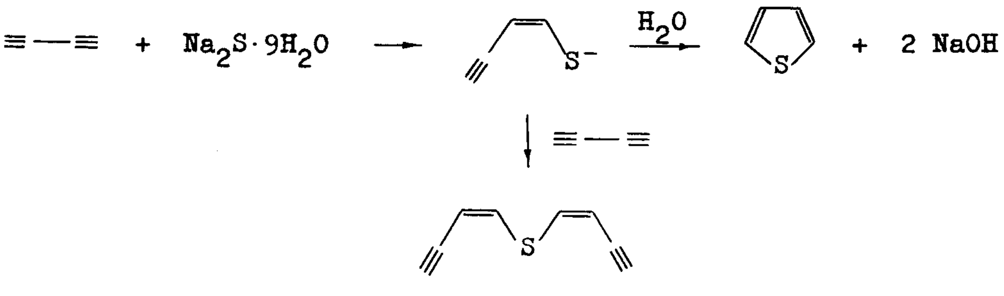
The reaction of hydrated sodium sulfide with the vinylacetylene system can be extended to vinylacetylenic sulfones where di(4-arylsulfonyl-1,2-dimethyl-1,3-butadienyl-1-) sulfides are formed.[113]

$$ArSO_2CH_2CH{=}C(Me)C{\equiv}CH + Na_2S\cdot 9H_2O \xrightarrow[H_2O]{EtOH}$$

$$\longrightarrow [ArSO_2CH{=}CH{-}C(Me){=}C(Me)]_2S$$

$$Ar = Ph, p\text{-}MeC_6H_4, p\text{-}ClC_yH_4, p\text{-}BrC_6H_4, p\text{-}NO_2C_6H_4$$

The reaction of sulfide ions with diacetylene has been observed.[114] Along with bis(2-ethynylvinyl) sulfide[115] a cyclic DVS analog, thiophene, was expected via cyclization of the intermediate 2-ethynylvinylthio anion or the corresponding thiol.



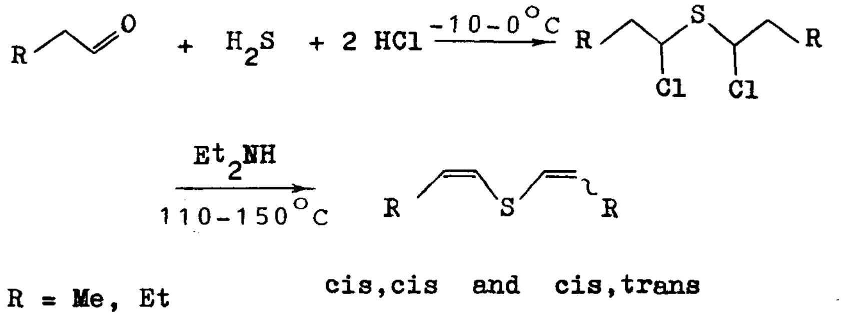
The synthesis of thiophene from diacetylene attempted previously by Schulte[116–118] can hardly be considered as preparative since the yield was no higher than 20 %.

A highly selective method for preparing thiophene in the KOH—DMSO medium in 94 % yield has been developed. The purity of the crude thiophene without any additional purification is 99.9 %.[114] This method can be used for commercial production of thiophene. The use of hydrogen sulfide instead of sodium sulfide is also possible.

It was also possible to direct the reaction of diacetylene with sulfide ion toward the formation of bis(2-ethynylvinyl) sulfide only (the yield is 90 % based on the acetylene consumed).[115] In this case liquid ammonia was used as the solvent, the sulfide ions being generated by ammonium sulfide formed in the reaction mixture from ammonia and hydrogen sulfide.

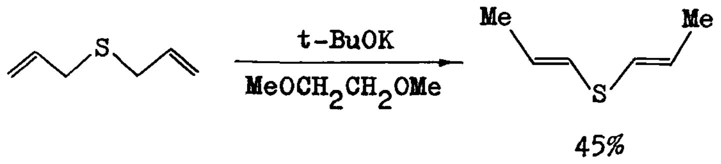
III.4. Synthesis of Di(1-alkenyl) Sulfides

Di(1-alkenyl) sulfides can be prepared in moderate yield (20–30 %) by condensation of aldehydes with hydrogen sulfide in the presence of HCl followed by dehydrochlorination of the α,α′-dichlorodialkyl sulfides formed.[13]



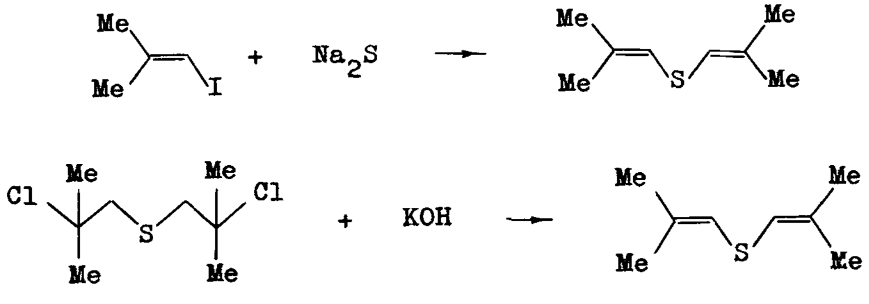
The synthesis of di(1-propenyl) sulfides by base-catalyzed isomerization of allyl sulfides is known.[119,120]

In the presence of potassium *t*-butoxide in 1,2-dimethoxyethane, diallyl sulfide isomerizes[119] exothermally.



In the presence of sodium *t*-butoxide the yield of di(1-propenyl) sulfide increases to 58 %. Also, with sodium ethoxide, the isomerization leads to di(1-propenyl) sulfide in 61 % yield, allyl 1-propenyl sulfide and 1,5-hexadiene-3-thiol appearing as by-products.[119]

A method for the preparation of di(2-methyl-1-propenyl) sulfide from 2-methyl-1-propenyl iodide and sodium sulfide[121] or di(2-methyl-2-chloropropyl-1) sulfide and alkali has been reported.[122]

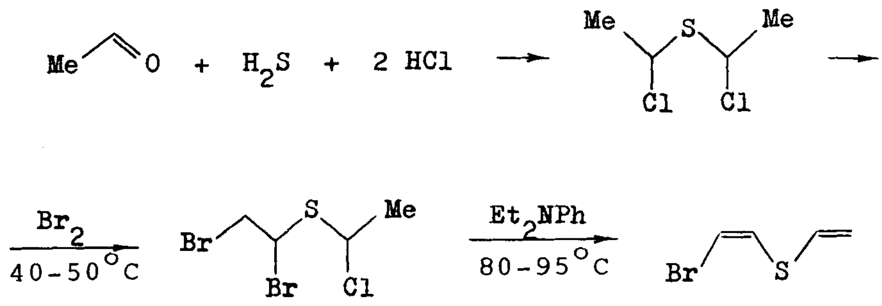


β-Substituted divinyl sulfides have been prepared in high yields from the corresponding α,α′-diiododialkyl sulfides by elimination of hydrogen iodide with trimethylamine.[123]

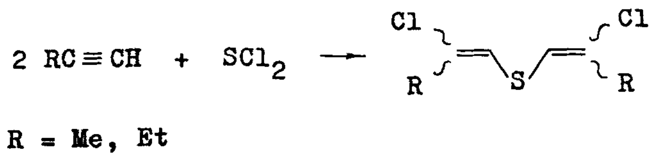
As shown above activated sulfide ions smoothly react with acetylenes containing electron-acceptor substituents. These substituents decrease the electron density at the terminal carbon atom of the acetylene group and facilitate the charge distribution upon anion attack thus favoring the nucleophilic addition.[124] On the other hand, the interaction of sulfide ions with acetylenes containing electron-donating substituents should be hindered. Indeed, 1-octyne fails to react with hydrated sodium sulfide under conditions suitable for the addition of sulfide ions to acetylene, phenylacetylene, diphenylacetylene, vinylacetylene, and diacetylene. Instead, the expected migration of the triple bond (the Favorsky isomerization[125]), leading to 2-octyne in quantitative yield, occurs. Thus, neither 1-octyne nor 2-octyne form the corresponding divinyl sulfides under the above conditions.

III.5. Synthesis of Functionalized Divinyl Sulfides

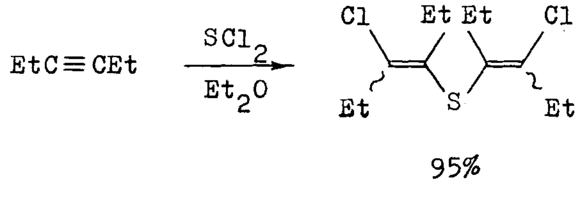
Monobromo substituted divinyl sulfide has been obtained[126] by a multi-step process from paraldehyde and hydrogen sulfide via the intermediate 1,1′-dichlorodiethyl sulfide which was brominated and then dehydrobrominated. The yield of vinyl 2-bromovinyl sulfide in the final step is 25–30 %.



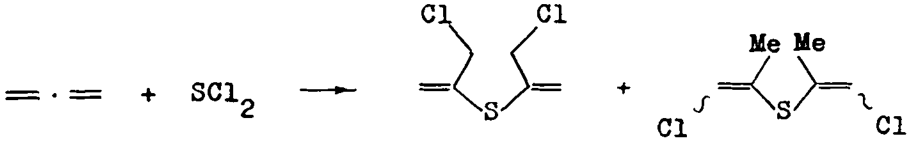
Di(2-chloro-1-propenyl) and di(2-chloro-1-butenyl) sulfide are formed in 80 % yield in the reactions of sulfur dichloride with the corresponding 1-alkynes.[127]



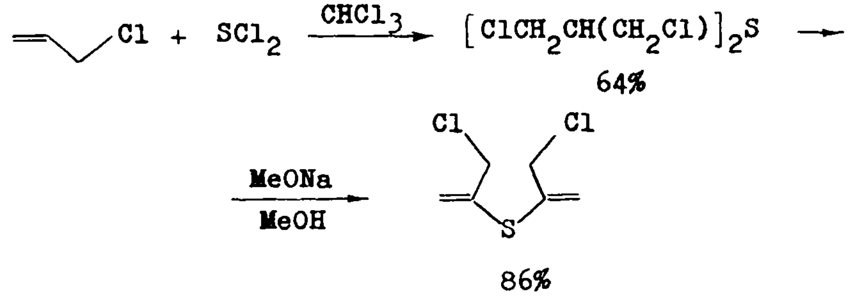
2-Hexyne reacts nearly quantitatively with SCl_2.[127]



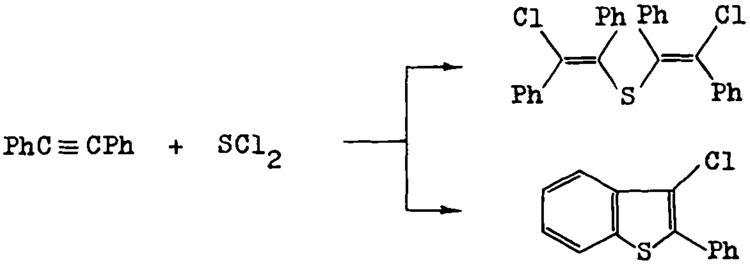
Sulfur dichloride adds to allene to form di(3-chloro-1-propenyl-2) sulfide and di(1-chloro-1-propenyl-2) sulfide.[128]



A synthetic route to di(3-chloro-1-propenyl-2) sulfide from di[2-chloro-1-(chloromethyl)ethyl] sulfide obtained by addition of sulfur dichloride to allyl chloride has been reported.[127]

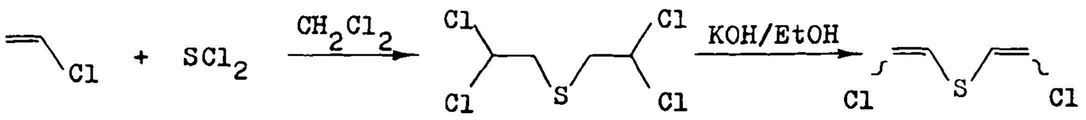


Diphenylacetylene and SCl_2 interact to form, depending on the reaction conditions, either the corresponding divinyl sulfide or 3-chloro-2-phenylbenz[*b*]thiophene.[127,129]

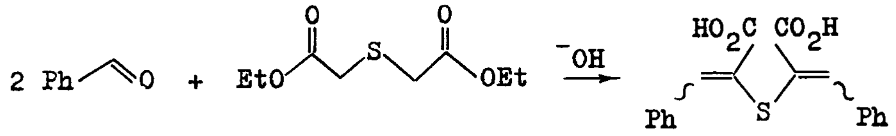


The orientation of the addition of SCl_2 to unsymmetric acetylenes depends on the solvent. However, the anti-Markovnikov adducts are formed in most cases.

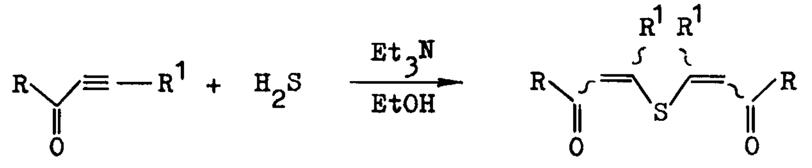
Sulfur dichloride adds to vinyl chloride[130] to give tetrachlorodiethyl sulfide. The dehydrochlorination of the latter leads to di(2-chlorovinyl) sulfide in 67–75 % yield.



Benzaldehyde reacts with di(carboethoxymethyl) sulfide in the presence of alkali according to the scheme:[131]

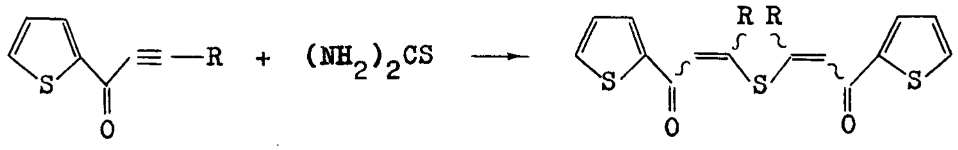


The reaction of α-ethynyl ketones with hydrogen sulfide in the presence of triethylamine gives di(ketovinyl) sulfides in 68–94 % yield.[132–134]



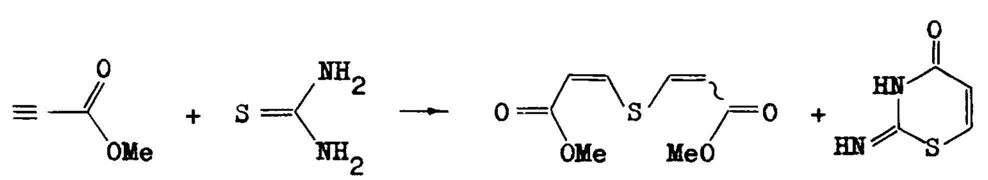
R = Me, Ph, 2-thienyl, 5-Br-2-thienyl; R^1=H, Bu, Ph, 2-thienyl, $C_6H_{13}S$

New substituted divinyl sulfides have been prepared by reaction of ethynyl ketones with thiourea in the presence of triethylamine.[135] According to ^{1}H NMR spectroscopic data 1,7-di(2-thienyl)-4-thiahepta-2,5-diene-1,7-dione is a *trans*, *trans*-isomer.

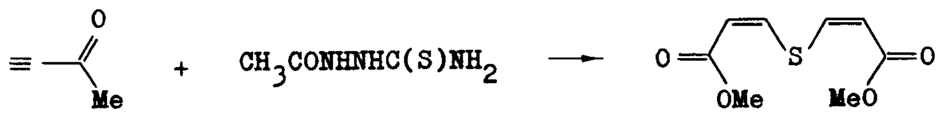


R = H, Bu, Ph, $C_6H_{13}S$

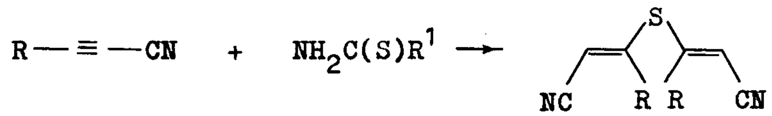
The reaction of thiourea with methyl propiolate in methanol yields a mixture of *cis,cis*- and *cis,trans*-di(2-carbomethoxyvinyl) sulfide along with a cyclic adduct.[136]



1-Substituted thiosemicarbazides, when treated with methyl propiolate, form an equimolar mixture of the *cis,cis*- and *cis,trans*-isomers of di(2-carbomethoxyvinyl) sulfide in 55 % yield.[137]

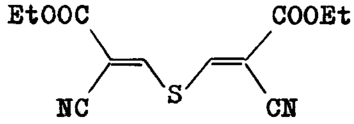


A method for preparing di(1-organyl-2-cyanovinyl) sulfides from substituted cyanoacetylenes and thiourea or ammonium dithiocarbamates is known.[138]



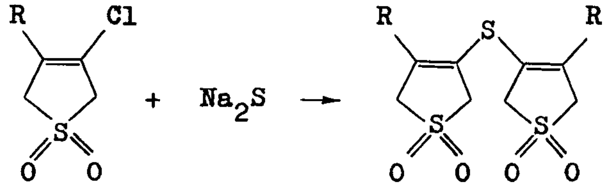
R = H, Alk, Ph; $R^1 = NH_2$, SNH_4

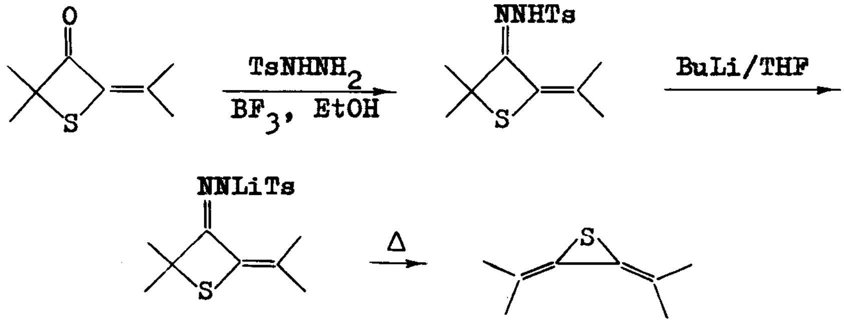
A process for obtaining substituted divinyl sulfides of the following structure has



been patented.[139,140]

The syntheses of the substituted divinyl sulfides shown below are reported in.[121,141]





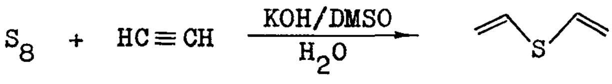
IV. SYNTHESIS OF DIVINYL CHALCOGENIDES AND THEIR DERIVATIVES BY REACTIONS OF CHALCOGENS WITH ACETYLENES

IV.1. Reaction of Sulfur with Acetylenes

Acetylene and sulfur in the presence of aromatic amines can give thiooxalic acid.[142,143] The reaction of photoexcited singlet $S(^1D)$ and triplet $S(^3P)$ sulfur atoms with acetylenes leads to thiophenes (via thiirenes, extremely unstable intermediates).[144–146]

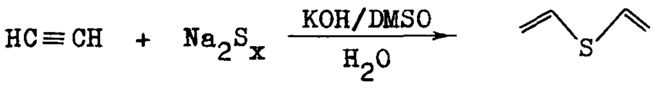
In the reaction of elemental sulfur with acetylene and its homologs as well as with activated acetylenes thiophene or its derivatives are formed.[145,147–150]

The reaction of acetylene and its derivatives with elemental sulfur in DMSO and HMPA, mainly leading to DVS (in 80 % yield), has been described.[45,151–153]



The reaction proceeds in the presence of alkali and involves undoubtedly the initial formation of the sulfide and polysulfides of the alkali metal which react further with acetylene as nucleophiles.

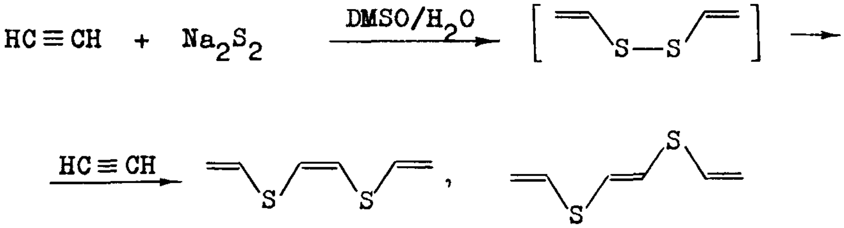
Cleavage of alkali di- and polysulfides (tri- and pentasulfides) by acetylene under pressure in superbasic media in the presence of water as the proton transfer agent has been studied.[154] The product of this reaction is DVS formed in 70–90 % yield (assuming that 1 mole of DVS is formed from 1 mole of polysulfide). A part of the alkali metal polysulfide acts as a reductant.



$x = 2\text{–}5$

The optimal molar ratio of polysulfide, solvent, and alkali is 1 : 12 : 4. The reaction temperature is 110–120 °C.

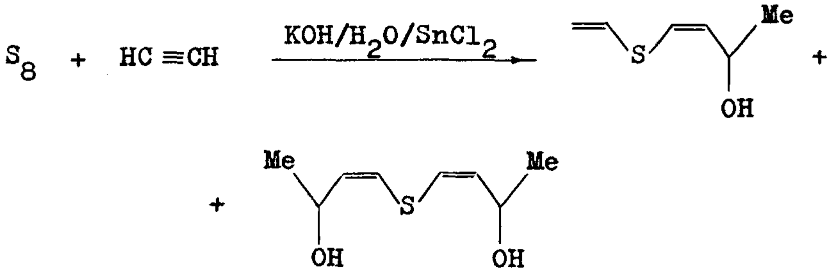
Under milder conditions, however, the reaction of sodium disulfide and acetylene gives, along with DVS, 1,2-di(vinylthio)ethene, as a mixture of *cis*- and *trans*-isomers (2 : 3), in approximately 10 % yield.[155]



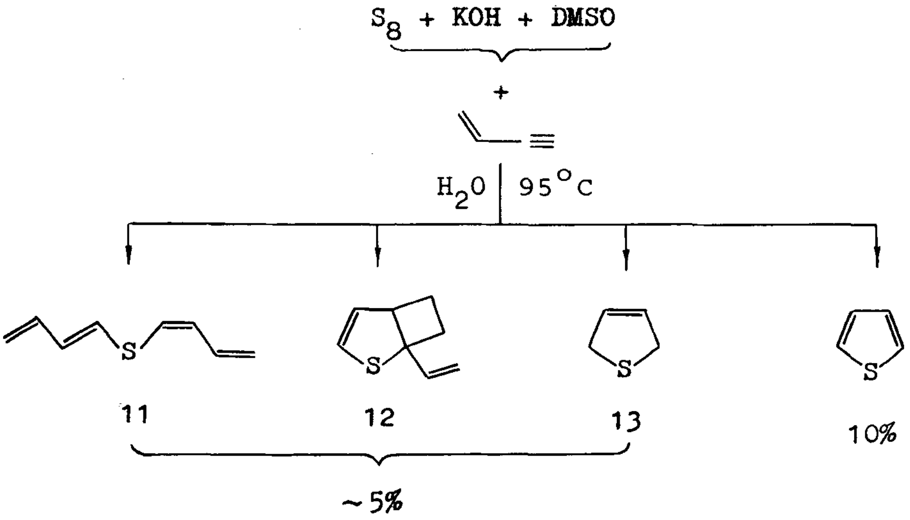
The di(vinylthio)ethenes seem to be formed from the intermediate divinyl disulfide by addition of the latter to acetylene. This reaction[156,157] is rather characteristic of organic disulfides.

The simplicity of the one-pot process, availability of the starting materials, and the fairly high yield of DVS make the present method very attractive for industrial purposes.

When the above reaction is carried out in an aqueous alkaline medium in the presence of tin chloride under an acetylenic pressure at 105–115 °C only traces of DVS are found in the reaction mixture, the reaction products being *cis*-1-vinylthio-1-buten-3-ol and *cis,cis*-di(3-hydroxy-1-butenyl) sulfide in a total yield of about 3 %.[45]

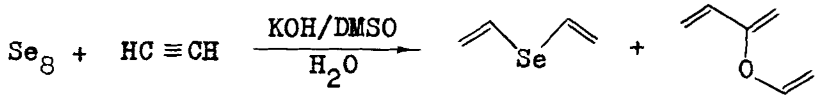


Vinylacetylene, when reacting with elemental sulfur in a superbasic medium, gives di(1,3-butadienyl-1) sulfide **11**, 1-vinyl-2-thiabicyclo[3.2.0]-3-heptene **12** and 2,5-dihydrothiophene **13**. Besides, thiophene was quite unexpectedly discovered in the reaction mixture in a yield almost twice exceeding the total yield of the compounds 11–13.[103,105,152,158]



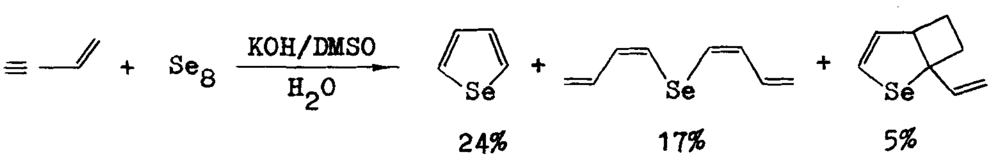
IV.2. Synthesis of Divinyl Selenides

IV.2.1. Reaction of acetylene with selenium The reaction of elemental sulfur with acetylene in a superbasic medium leading to DVS has been extended to elemental selenium.[159,160] From selenium and acetylene in aqueous DMSO in the presence of KOH at 95–120 °C, divinyl selenide and 2-vinyloxy-1,3-butadiene, the product of a parallel hydration-trimerization of acetylene are formed. The yield of divinyl selenide is 26 %.[159]



When the reaction is carried out in HMPA the yield of divinyl selenide rises to 58 %[72], reaching 79 %[45] in the case of an aqueous alkaline medium with $SnCl_2$ as a reductant. *cis*-1-Vinylseleno-1-buten-3-ol, *cis,cis*-di(3-hydroxy-1-butenyl) selenide and selenophene are formed as by-products.[45,161] The conditions allowing the reaction to be directed towards the predominant formation of *cis*-1-vinyl-seleno-1-buten-3-ol in a yield of up to 50 % have been found.

IV.2.2. Reaction of vinylacetylene with selenium The reaction of acetylene with elemental selenium has been extended to vinylacetylene.[72,105,152,158,162,163] In the presence of the superbasic catalytic systems KOH-DMSO and KOH-HMPA at 100–120 °C vinylacetylene reacts with selenium to form selenophene, di(1,3-butadienyl-1) selenide and 1-vinyl-2-selenabicyclo[3.2.0]-3-heptene.[162]

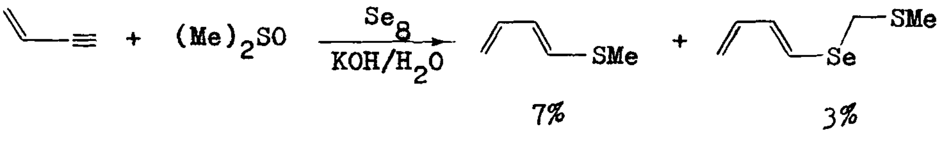


The yields of selenium-containing products are calculated relative to the selenide ion[164] formed according to the following scheme:

$$3Se + 6OH \longrightarrow 2Se^{2-} + SeO_3^{2-} + 3H_2O$$

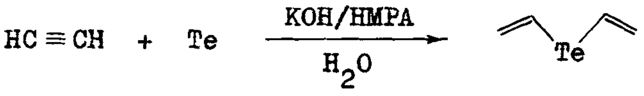
Water is added to the reagents in equimolar quantities relative to acetylene and serves as the proton donor.

Methyl 1,3-butadienyl-1 sulfide and methylthiomethyl 1,3-butadienyl-1 selenide were also isolated from the reaction mixture. Here vinylacetylene behaves as a trap for the methanethiolate and methylthiomethaneselenolate anions formed by reaction of selenium and alkali with DMSO.[165]

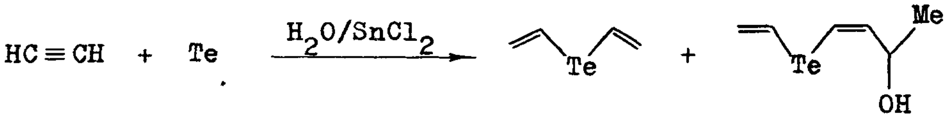


IV.3. Synthesis of Divinyl Telluride

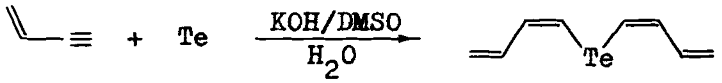
IV.3.1. Reaction of acetylene with tellurium The reaction of acetylene and elemental tellurium in the presence of KOH in aqueous aprotic dipolar solvents (DMSO, HMPA, tetrahydrofuran, ethyleneglycol dimethyl ether, diethyleneglycol divinyl ether) gives divinyl telluride:[166,167]



In the KOH—HMPA system the conditions affording divinyl telluride in 54 % yield have been found. The reaction runs at 110–120 °C in the presence of water under acetylene pressure. When this reaction is carried out without HMPA in an aqueous alkaline medium with $SnCl_2$ the yield of divinyl telluride amounts to 94 %. *cis*-1-Vinyltelluro-1-buten-3-ol is formed as a by-product in approximately 5 % yield.[48]



IV.3.2. Reaction of vinylacetylene with tellurium Elemental tellurium in aqueous DMSO at a temperature of 100 °C and a Te: KOH ratio of 1 : 1.5 reacts with acetylene to form a multicomponent mixture containing di(1,3-butadienyl-1) telluride as the main product (54 % as determined by GLC).[158] The yield of the latter is 7 % (based on the amount of tellurium employed).

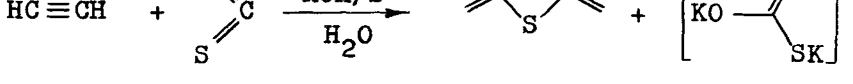


V. SYNTHESIS OF DIVINYL SULFIDE AND ITS DERIVATIVES BY REACTIONS OF THIO COMPOUNDS WITH ACETYLENES

In a series of recent studies[94,168–177] it was attempted to develop "mercaptan-free" one-step methods for the synthesis of DVS and alkyl vinyl sulfides from cheap thiono compounds. With this aim in view there was undertaken a systematic investigation of the reactions of acetylene with simple thiono compounds such as carbon disulfide,[171] sodium thiosulfate,[172] thiourea,[54,173,174] and esters of various thioacids[175–177] including thiophosphoric acids.[168]

V.1. Reaction of Carbon Disulfide with Acetylene

The reaction of carbon disulfide with acetylene and alkali in aqueous DMSO and HMPA affords DVS in 97 and 43 % yield, respectively.[171]



S = DMSO, HMPA

The reaction proceeds at 140–160 °C under acetylene pressure (the $CS_2:KOH:H_2O$ ratio is 1 : 2 : 3) and is accompanied by formation of polymeric products due to the anionic polymerization of acetylene and the copolymerization of the latter with carbon disulfide. At a temperature of 200 °C the process is vigorous with not unfrequent explosions. Upon decreasing the temperature to 110–120 °C the yield of DVS drops sharply (to as low as 6 %). The alkali concentration affects greatly the yield of DVS. In the absence of KOH no DVS is formed, the reaction leading to polymeric products only. At CS_2 : KOH ratios of 1 : 0.5 and 1 : 1, the yield of DVS is 22 and 30 %, respectively. With three-fold excess of alkali a strong resinification takes place and only at CS_2 : KOH = 1 : 2 the yield of DVS is near quantitative.

High yields of DVS require a considerable excess (almost ten-fold) of acetylene over carbon disulfide. Lower concentrations of acetylene decrease the yield of DVS and lead to resinous products.

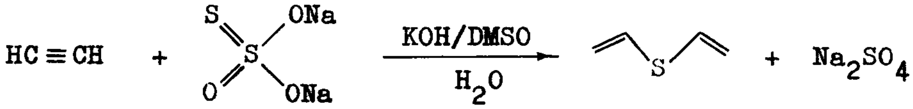
In an aqueous medium with large excess of alkali (3-fold with respect to carbon disulfide), the reaction can be directed to the formation of products of the polycondensation of acetylene with carbon disulfide. Thus, at 120–130 °C the polymer yield is 63 % and 91 % at 150–160 °C.

The polymer is dark ruby, readily soluble in most organic solvents (CCl_4, $CHCl_3$, diethyl ether, slightly less soluble in ethanol) and insoluble in water, easily forms films and displays paramagnetic and electroconductive properties.

When carried out in DMSO, but without alkali, the reaction of carbon disulfide with acetylene gives another polymer which is a black powder insoluble in organic solvents. This polymer also exhibits paramagnetic properties.

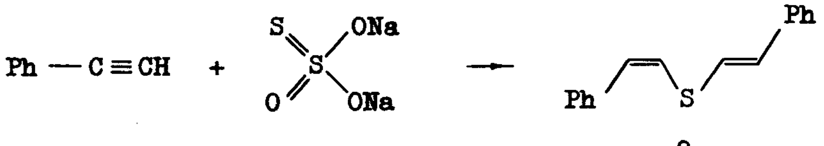
V.2. Reaction of Sodium Thiosulfate with Acetylenes

In the reaction of sodium thiosulfate with acetylene[172] in the KOH—DMSO—H_2O system at 110–120 °C the yield of DVS is 15 %.



Increasing the reaction temperature to 135 °C allows to obtain DVS in a yield of about 40 %, methyl vinyl sulfide and dimethyl sulfide being formed as by-products. When the reaction is performed at 165–175 °C during 4 hours strong resinification of the reaction mixture occurs and the DVS yield decreases to 4 %. In this case, dimethyl sulfide and methyl vinyl sulfide become the main reaction products. They result from oxidation-reduction processes involving DMSO and the reactions of DMSO with acetylene.[44,49] With a much shorter reaction time, however, even at higher temperature (210 °C, for example) DVS can be prepared[72] in yields not higher than 40 %, the yields of methyl vinyl sulfide and dimethyl sulfide not exceeding 4 % (based on the starting amount of DMSO). The reaction mixture is readily separated by distillation.

The reaction of sodium thiosulfate with phenylacetylene in the KOH—DMSO—H_2O system at a temperature of 165–175 °C leads to *cis,trans*-bis(2-phenylvinyl) sulfide **9** in 37 % yield.

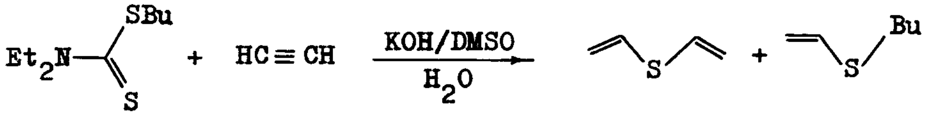


9

V.3. Reaction of Thionic Acid Esters with Acetylenes

In order to develop further methods for preparing DVS and its derivatives the reactions of acetylenes with other thionic systems possessing a C=S group bound to heteroatoms (O, S, N, P) have been studied.

V.3.1. Reaction of thiocarbamates with acetylene The reaction of acetylene and *N,N*-diethyldithiocarbamic acid *S*-butyl ester in DMSO in the presence of water and equimolar quantities of alkali (relative to dithiocarbamate) affords DVS and butyl vinyl sulfide (in 68 and 93 % yield, respectively), the reaction temperature is 120 °C.[175]



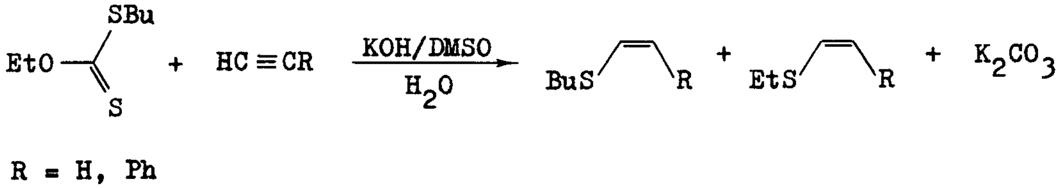
The reaction also proceeds with even smaller quantities of alkali (1 mole per 5 moles of dithiocarbamate). However, the yield of DVS and alkyl vinyl sulfide decreases to one third to one fifth in this case. The total product balance unambiguously shows that DVS is mainly formed from the thione component only whereas butyl vinyl sulfide results from base catalyzed cleavage of the C—S bond in the presence of acetylene.

A number of examples of acetylene-stimulated base-catalyzed cleavage of the C—S bond are known.[178] Thus, different 2-hydroxyalkyl sulfides (2-(ethylthio)ethanol,[179,180] di(2-hydroxyethyl) sulfide,[181,182]), 2-vinyloxyalkyl sulfides, and di(2-mercaptoethyl) sulfide[181] undergo cleavage at the C—S bond in the presence of acetylene to form the corresponding unsaturated sulfides along with vinylation products.

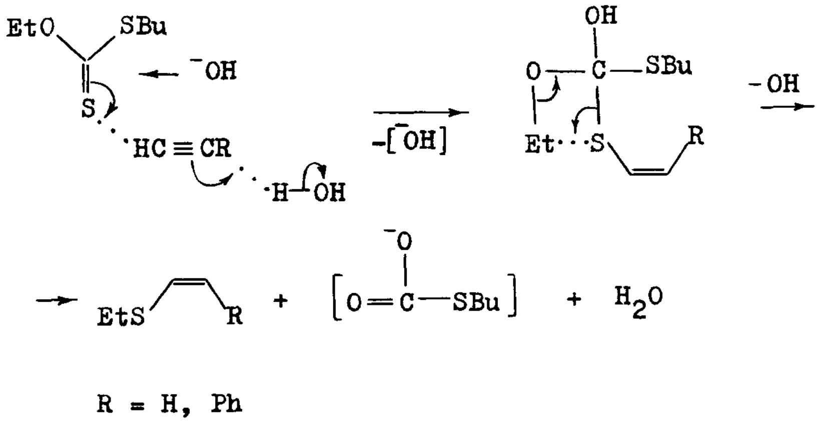
The reaction of *N,N*-diethyldithiocarbamic acid esters with acetylene allows one to obtain in almost quantitative yield alkyl vinyl sulfides together with DVS by a "mercaptan-free" process. Moreover, the extension of the above reaction to various dithiocarbamic acid *S*-vinyl esters substituted in the vinyl group provides a simple route to unsymmetrically substituted divinyl sulfides.[176]

V.3.2. Reactions of thiocarbonic acid esters with acetylenes The reactions of various thiocarbonic acid esters with acetylenes in superbasic media lead to DVS and its derivatives along with organyl vinyl sulfides, frequently involving migrations of groups from the oxygen atom to the thiono sulfur.

In the interaction of acetylenes and *O*-ethyl *S*-butyl dithiocarbonate (aqueous DMSO, KOH, 125–135 °C), along with butyl vinyl sulfides (yields of up to 76 %), ethyl vinyl sulfides are formed (yields 50–53 %).[177]

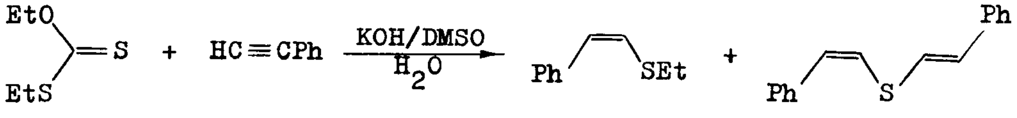


The formation of ethyl vinyl sulfides indicates a rearrangement according to the following suggested scheme:[177]



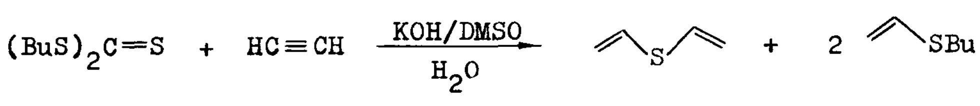
In the case of phenylacetylene,[177] butyl and ethyl (2-phenylvinyl) sulfide with *cis*-configuration and *cis,trans*-di(2-phenylvinyl) sulfide **9** (13 % yield) are formed.

The reaction of *O*-ethyl *S*-ethyl dithiocarbonate with phenylacetylene in the KOH-DMSO-H_2O system at 135 °C affords *cis*-ethyl (2-phenylvinyl) sulfide in a yield considerably exceeding the stoichiometric amount (128 %) if it is put that 1 mole of ethyl (2-phenylvinyl) sulfide should be formed from 1 mole of *O*-ethyl *S*-ethyl dithiocarbonate. This fact gives evidence for the following rearrangement: the ethyl group required for the formation of ethyl (2-phenylvinyl) sulfide is derived from the OEt group.



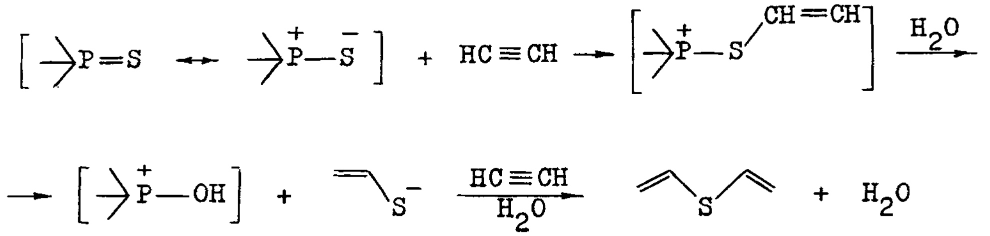
In this case also *cis*,trans-bis(2-phenylvinyl) sulfide **9** is formed, the yield is 22 %.

Dibutyl trithiocarbonate reacts with acetylene in aqueous DMSO in the presence of an equimolar amount of KOH to form DVS and butyl vinyl sulfide in 24 and 68 % yield, respectively.



The reaction takes place at a temperature of 135 °C. The yield of butyl vinyl sulfide is calculated on the assumption that 1 mole of trithiocarbonate gives 2 moles of butyl vinyl sulfide.

V.3.3. Reactions of thiophosphoric esters with acetylene In the reaction of thionophosphates with acetylene in aqueous DMSO in the presence of alkali DVS is formed.[168]

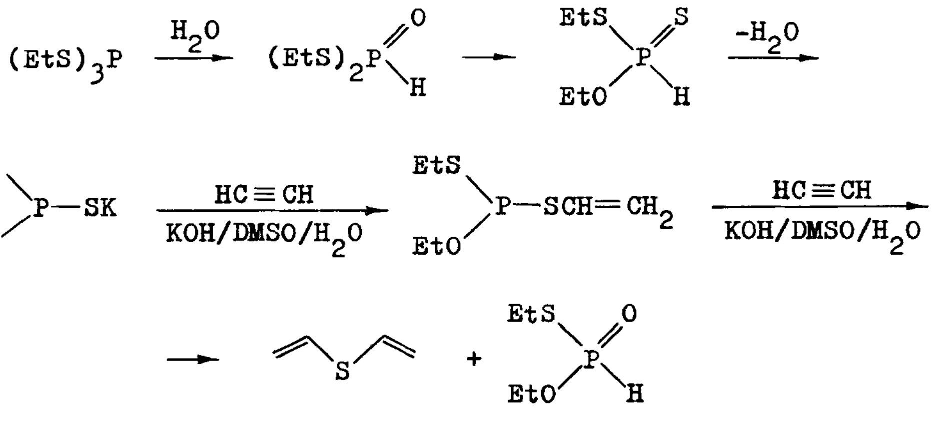


Upon treatment of *O,O,O*-triethyl thiophosphate and triethyl tetrathiophosphate with acetylene along with DVS, ethyl vinyl ether and ethyl vinyl sulfide were obtained[168] in 10–24 and 56 % yield, respectively, due to alkali-induced cleavage of P—O and P—S bonds in the presence of acetylene. Without alkali as well as with an equimolar ratio of potassium hydroxide and *O,O,O*-triethyl thiophosphate the reaction does not take place. Excess alkali is necessary since in the reaction of the thiono fragment with acetylene and upon cleavage of the P—O bond KOH is quenched by the phosphoric acids formed.

With the reaction temperature rising from 80 to 140 °C the yield increases more than 4-fold, reaching 80 %.[168]

The yield of DVS from triethyl tetrathiophosphate is only two third of that from *O,O,O*-triethyl thiophosphate (this reaction also proceeds in HMPA). The yield of ethyl vinyl sulfide is 56 % (assuming that 1 mole of the starting tetrathiophosphate gives 3 moles of ethyl vinyl sulfide).

Triethyl trithiophosphite reacts with acetylene to form ethyl vinyl sulfide in 70 % yield. Unexpectedly, a considerable amount of DVS was found in the reaction mixture in a yield of about 100 % based on the triethyl trithiophosphite initially present. The appearance of DVS is explained[178] by the hydrolysis of triethyl trithiophosphite to dialkyl dithiophosphite which can react with acetylene in the thiono form.



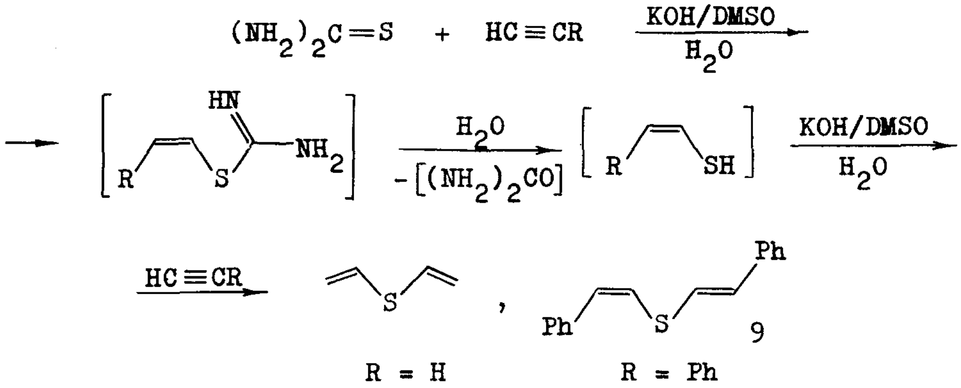
The hydrolysis of trialkyl phosphites is known[183] to lead first to dialkyl phosphites. The formation of the intermediate *O,S*-dialkyl dithiophosphite is confirmed by the presence in the reaction mixture of ethyl vinyl ester (in 10 % yield) and traces of hydrogen sulfide. Small amounts of DVS (~20 %) also have been prepared by the reaction of triethyl thiophosphite with acetylene in HMPA.

Thus, DVS is formed from the P=S fragment of esters of various thiophosphoric acids and acetylene in superbasic media.

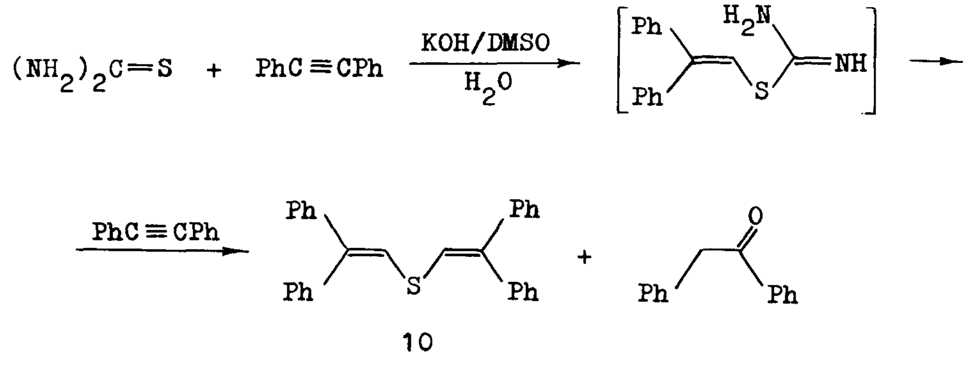
V.4. Reaction of Thioureas with Acetylenes

In superbasic systems thiourea has been shown[94,173,174,176] to react with both acetylene and its mono- and diphenyl derivatives.

The reaction occurs in DMSO or HMPA in the presence of alkali and small amounts of water at 90–140 °C.[94] The interaction does not stop at the step of the monoadduct formation, but proceeds to the formation of DVS and its phenyl derivatives.[9,10]



In the case of diphenylacetylene a rearrangement leading to bis(2,2-diphenylvinyl) sulfide **10** is observed. A considerable amount (up to 35 %) of phenyl benzyl ketone is formed as well.



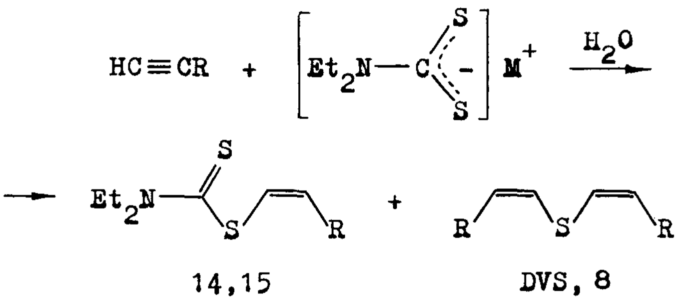
In the absence of water it was possible to isolate in small yield the primary monoadduct, *S*-(diphenylvinyl)isothiourea.[94] The yield of divinyl sulfides depends on the reaction conditions and the acetylene employed. Under optimal conditions DVS, *cis,trans*-bis(2-phenylvinyl) sulfide **9** and *bis*(2,2-diphenylvinyl) sulfide **10** were obtained (from thiourea and the corresponding acetylenes) in 84, 44, and 17 % yields, respectively.

VI. REACTIONS OF THIOACID SALTS WITH ACETYLENES

VI.1. Reactions of Dithiocarbamate Ions with Acetylenes

The first successful attempts of nucleophilic addition of *N,N*-dialkyldithiocarbamic acid anions to acetylenes have briefly been reported in.[176,184–187]

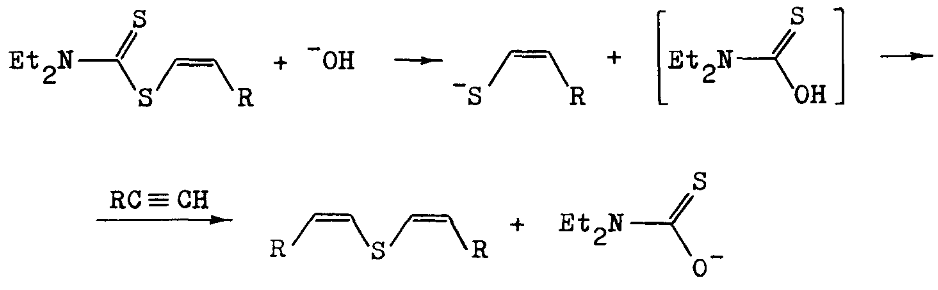
The reaction was carried out in polar aprotic solvents: DMSO, HMPA, THF, and dioxane containing 1–6 % water (by weight). The reaction products are the corresponding *S*-vinyl *N,N*-dialkyl dithiocarbamates (**14**, **15**) and divinyl sulfides (DVS, **8**).[188]



14,15 DVS, 8

R = H (14, DVS), Ph (15, 8); M = Na, K

The highest yield of the adducts **14** and **15** (53 and 36 %, respectively) is observed in THF. Divinyl sulfides (DVS, **8**) are secondary products resulting from the alkaline solvolysis of the adducts **14** and **15**, followed by nucleophilic addition of ethenethiolate anions to a second molecule of acetylene:

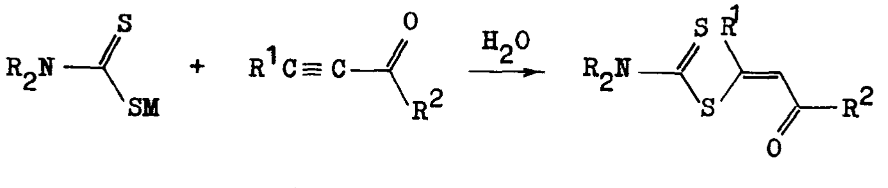


R = H, Ph

The divinyl sulfides (DVS, **8**) may become main products. They are formed especially readily in DMSO. In the presence of equimolar amounts of KOH at 150 °C sodium *N,N*-diethyldithiocarbamate reacts with acetylene to form DVS in quantitative yield.[188]

Furthermore, under these conditions the thiono sulfur also begins to react with acetylene to form DVS since the DVS yield exceeds the stoichiometric one (by approximately 30 %).

The reaction of alkali metal *N*,*N*-dialkyldithiocarbamates with substituted ethynyl ketones (3-phenyl-1-propyn-3-one, 1-phenyl-1-butyn-3-one and 1,3-diphenyl-1-propyn-3-one) in the presence of water gives the corresponding substituted *S*-vinyl *N*,*N*-dialkyl dithiocarbamates in quantitative yield.[189] The reaction readily proceeds in the biphasic system water-diethyl ether at 20–25 °C.



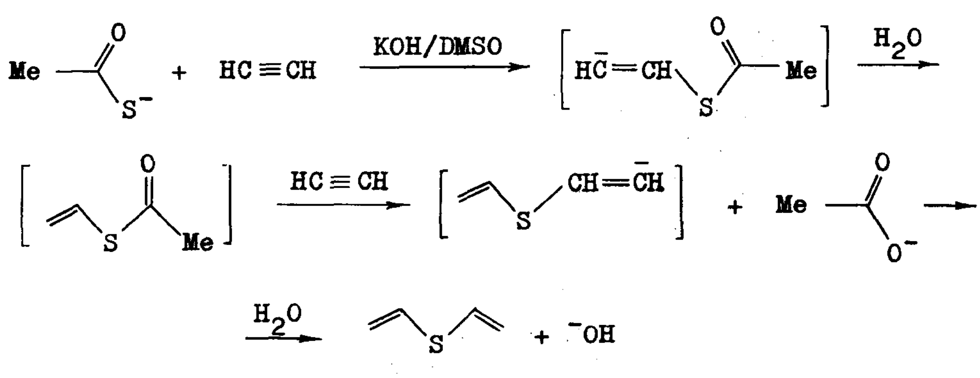
R = Me, Et; R^1= H, Ph; R^2= Me, Ph; M = Na, K

VI.2. Reaction of the Thioacetate Anion with Acetylenes

In order to check the generality of reactions between salts of *N*,*N*-dialkyldithiocarbamic acids and acetylene an attempt was made to carry out the addition of the activated thioacetate anion to acetylene using superbasic systems with aprotic dipolar solvents, crown ethers, and related complexing agents under both homogeneous and biphasic conditions.[190]

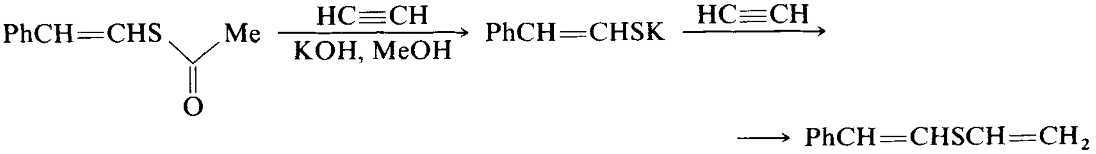
Some unsuccessful attempts at addition of thioacetic acid to acetylene to obtain vinyl thioacetate are known.[191,192] It was suggested[192] that no smooth addition of thioacetic acid to acetylene could be achieved under nucleophilic conditions due to the low nucleophilicity of the thioacetate anion. However, it became possible to add thioacetic acid to phenylacetylene by simultaneous initiation of the reaction with peroxides and UV irradiation.[193,194]

The reaction between the thioacetate anion and acetylene in a superbasic medium (KOH—DMSO, KOH—HMPA) with small amounts of water at 130–140 °C gives DVS[195] in about 60 % yield.



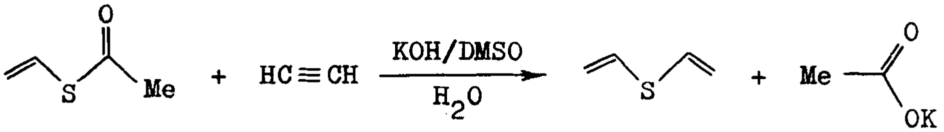
The reaction was carried out with two-fold excess of alkali over thioacetic acid. The reactants start to interact slowly at 80 °C. The process also runs in other solvents (*N*,*N*-dimethylformamide, dioxane) though with considerably lower yields of DVS.

A method for the preparation of α, β-unsaturated sulfides by alkali-induced cleavage of the thioacetate C—S bond in excess alkali is know.[196] This process allows one to synthesize vinyl sulfides with even a norbornene moiety in spite of the unstability of the corresponding mercaptans.[197] In aprotic dipolar solvents (DMSO, HMPA) the reaction proceeds at moderate temperatures and atmospheric pressure.[198] By the above method vinyl (2-phenyl-vinyl) sulfide was obtained in 50 % yield from S-(2-phenylvinyl) thioacetate and acetylene in the presence of alcoholic alkali.[197]



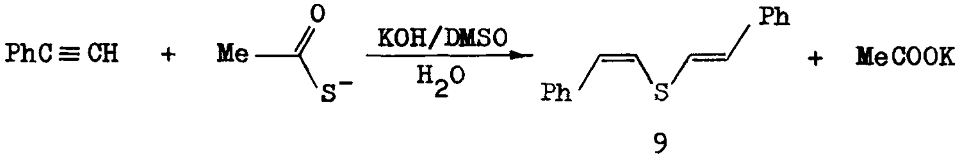
$$\mathrm{PhCH{=}CHS\underset{\underset{O}{\|}}{C}Me} \xrightarrow[\text{KOH, MeOH}]{\mathrm{HC{\equiv}CH}} \mathrm{PhCH{=}CHSK} \xrightarrow{\mathrm{HC{\equiv}CH}} \mathrm{PhCH{=}CHSCH{=}CH_2}$$

The reaction of S-vinyl thioacetate with acetylene has been reported.[190] The above reagents readily interact in aprotic dipolar solvents to form DVS via cleavage of the (O)C—S bond.



The experiments were carried out under comparable conditions: 130–140 °C, 4 hours, S-vinyl thioacetate:H_2O:KOH = 0.02:0.1:0.04 (mole), 75 ml solvent. Acetylene was supplied in large excess under a pressure of 10–15 atm. In DMSO the yield of DVS was 92 %. Along with DVS, however, methyl vinyl sulfide and dimethyl sulfide, the products of the reaction of acetylene with DMSO, were identified by GLC.[49] In HMPA, DMF, and dioxane the DVS yields are 66, 68, and 85 %, respectively.

In the superbasic KOH—DMSO medium the addition of the thioacetate anion to phenylacetylene proceeds in the same manner with formation of *cis,trans*-bis(2-phenylvinyl) sulfide **9** in 57 % yield.[190]

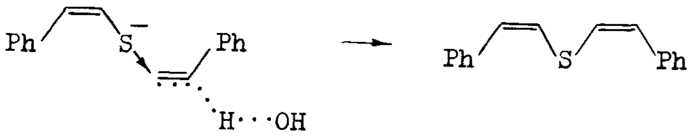


9

The reaction was performed at 120–130 °C for 10 hours with a three-fold excess of phenylacetylene. The structure of **9** has been confirmed by ^1H NMR and IR spectroscopy and dipole moment measurements. The data obtained are in full agreement with those of **9** prepared independently.

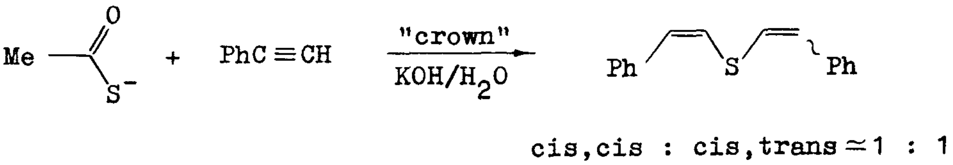
In the superbasic system consisting of TEPO and KOH the thioacetate anion adds to phenylacetylene in the presence of small quantities of water to form *cis,cis*-bis(2-phenylvinyl) sulfide **8** in 90 % yield.[77]

The stereochemistry of the reaction of the thioacetate anion with phenylacetylene in TEPO is quite different from that in DMSO. The formation of *cis,cis*-bis(2-phenylvinyl) sulfide **8** shows that the second stage of this reaction also proceeds as a "normal" *trans*-addition.



It is possible that in TEPO, due to its specific solvating properties the saponification of the intermediate (2-phenylvinyl) thioacetates does not involve phenylacetylene. As a result, 2-phenylethenethiolate anions act as kinetically independent nucleophilic species and, consequently, should add to phenylacetylene in the usual way.

In search for new routes to activation of weakly nucleophilic anions such as the thioacetate anion the reaction of phenylacetylene with the thioacetate anion in the presence of dibenzo-18-crown-6 at 70–80 °C in an aqueous-organic medium has been performed, phenylacetylene serving as the organic phase.[190]

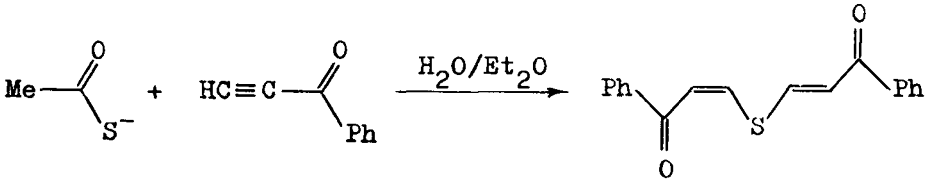


The yield of bis(2-phenylvinyl) sulfide is 72 % whereas in the experiments carried out without the crown ether the yield was as low as 20–22 % under the same conditions.

Triethylbenzylammonium chloride (TEBA) in a two-phase system also catalyzes the addition of the thioacetate anion to phenylacetylene, although less efficiently than crown ether. Under comparable conditions the product yield was 37 %, the *cis,cis*- and *cis,trans*-isomer ratio being approximately 1:1.[190]

The reaction of the thioacetate anion with phenylacetylene has shown for the first time that an acceleration of the addition of weak nucleophiles to the triple bond in biphasic catalytic systems is possible. The results obtained[190] indicate that the use of cyclic polyethers and tetraorganylammonium salts in acetylene chemistry may provide preparative advantages of a general character.

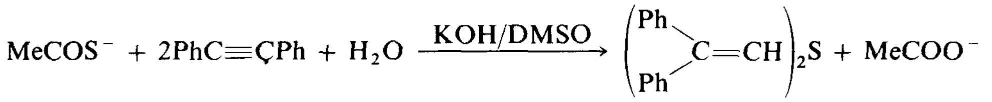
The nucleophilic addition of the thioacetate anion to 3-phenyl-1-propyn-3-one proceeds almost quantitatively under mild conditions leading to the only product, *cis,trans*-di(2-benzoylvinyl) sulfide in 90 % yield.[190] The reaction was carried out in aqueous ether (two-phase system) at room temperature during 2 hours.



Vinylacetylene readily reacts with potassium thioacetate in the presence of KOH, even at 90 °C.[190] The reaction products are di(1,3-butadienyl-1) sulfide **11**, 1-vinyl-2-thiabicyclo[3.2.0]-3-heptene **12** and 2,5-dihydrothiophene.

The yield of di(1,3-butadienyl-1) sulfide **11** is 40 %, those of the two other products being 3-5 %. With excess vinylacetylene the reaction may be directed towards the formation of **11** as the only product.[190] The yield of **11** approaches 66 % under these conditions.[190]

The reaction of potassium thioacetate with diphenylacetylene, when carried out in aqueous DMSO at 140–150 °C for 15 hours and $MeCOSH:PhC{\equiv}CPh:H_2O:KOH = 1:3:5:5$ (mole), affords bis(2,2-diphenylvinyl) sulfide **10** in 57 % yield.[190] The sulfide **10** is isolated from the reaction mixture by recrystallization.



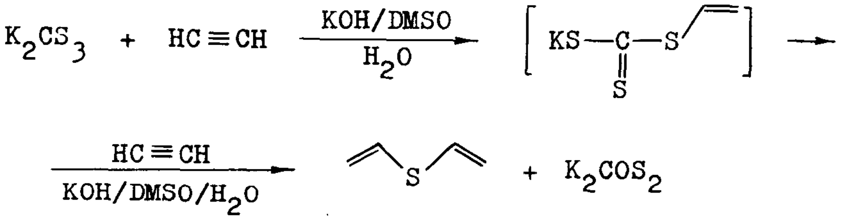
$$MeCOS^- + 2PhC{\equiv}CPh + H_2O \xrightarrow{KOH/DMSO} (Ph_2C{=}CH)_2S + MeCOO^-$$

10

In the case of distillation of the reaction mixture, instead of **10** tetraphenylthiophene, formed by oxidation of bis(2,2-diphenylvinyl) sulfide with DMSO or atmospheric oxygen, is isolated.[96,199]

VI.3. Reaction of the Trithiocarbonate Anion with Acetylene

At 90 °C potassium trithiocarbonate reacts with acetylene in KOH-DMSO with a small amount of water added to form DVS in 84 % yield.[200]



Elevation of the temperature to 130 °C increases the DVS yield two-fold which is explained by involvement of a second sulfur atom in the reaction. At 200 °C the DVS yield decreases sharply due to resinification.

VII. PROPERTIES, REACTIONS, AND APPLICATIONS OF DIVINYL SULFIDE

Until recently DVS was unavailable and, therefore, a little studied compound. The development of simple and commercially feasible methods for preparing DVS has allowed systematic investigations of its physicochemical properties and reactivity. At present addition, substitution, oxidation, heterocyclization, Diels-Alder, carbenylation, polyaddition, and polymerization reactions of DVS are under detailed investigation.

VII.1. Physical Properties of Divinyl Sulfide

Divinyl sulfide is a labile, volatile, transparent, colorless liquid with a faint specific odor, b.p. 83–84 °C/720 mm, n_D^{20} 1.5018, d_4^{20} 0.9093; it mixes in all ratios with most organic solvents; the solubility in water is approximately 1 g/l.

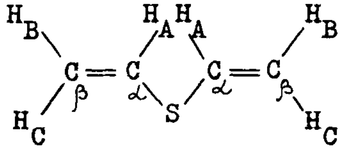
Dipole moment (D, benzene, 25 °C) 1.07:[201], 1.20[202]; IR spectrum (cm^{-1}, neat liquid): 3105 w, 3030 w, 3008 w (ν_{CH}), 1590 sh, 1584 ($\nu_{C=C}$); 1382 m ($\delta_{=CH_2}$), 1276 m ($\delta_{(CH)_2}$), 1036 m, 1014 m (ρ_{CH_2}), 960 s (τ_{CH_2}), 901 sh, 880 s (ω_{CH_2}), 735 m, 728 m, 685 m, 615 m(ν_{CSC}), 592 s, 610 m ($\omega_{(CH)_2}$).[201,203]

The Raman spectrum of DVS crystals[204] contains bands (cm^{-1}): 1590 ($\nu_{C=C}$), 1387 (δ_{CH_2}), 1285 (δ_{CH}), 715 (ν_{CSC}), in the liquid and glassy state the $\nu_{C=C}$ and ν_{CSC} vibrations are represented by the following triplets (cm^{-1}): 1599, 1592, 1584 and 734, 721, 684.

UV spectrum[203,205] (ν_{max}, cm^{-1}, $E \cdot 10^{-3}$): 50160, sh 47000, sh 45400, 42320, 39160 (vapor), sh 46480 (4.3), 41320 (8.4), 38560 (7.4) in hexane; sh 46000 (4.3), 41680 (7.9), 38840 (6.9) in ethanol; sh 46000 (4.0), 41800 (7.8), 38640 (6.0) in dioxane.

The first adiabatic ionization potential of DVS is 8.25 eV.[206]

^1H and ^{13}C NMR spectra of DVS[207,208](δ, ppm, J, Hz, CCl_4, TMS):

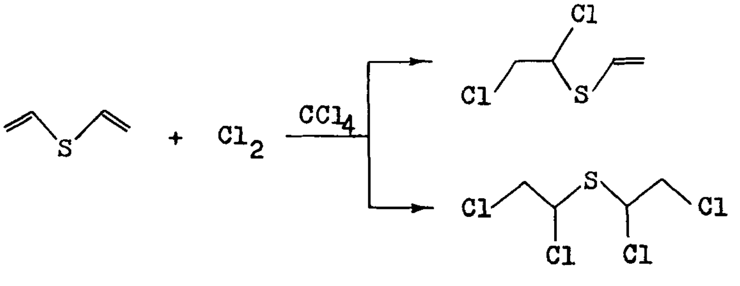


6.39 (H_A), 5.26 (H_B), 5.26 (H_C), 129.88 (C_α), 114.34 (C_β), $J_{H_AH_B}$ 9.6, $J_{H_AH_C}$ 16.8, $J_{C_\alpha H_A}$ 172.0, $J_{C_\beta H_B}$ 162.0, $J_{C_\beta H_C}$ 159.6.

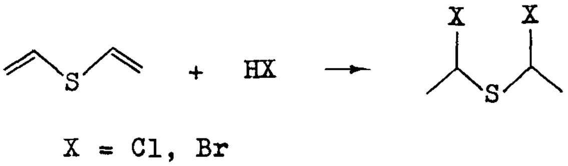
From the IR and Raman spectra the authors[204] have concluded that two DVS rotamers are stable within the range from −196 to 100 °C, these are *trans,trans* (which is present in the crystalline state) and *cis,trans*. According to the conformational analysis,[204] dipole moments, and IR spectra,[201,203] however, the twisted *trans,trans*-conformation of DVS is the most populated one.

VII.2. Reactions with Electrophiles

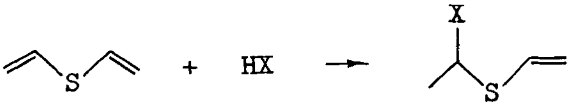
Chlorine readily adds to DVS at one or both double bonds to form 1,2-dichloroethyl vinyl sulfide or bis(1,2-dichloroethyl) sulfide.[209]



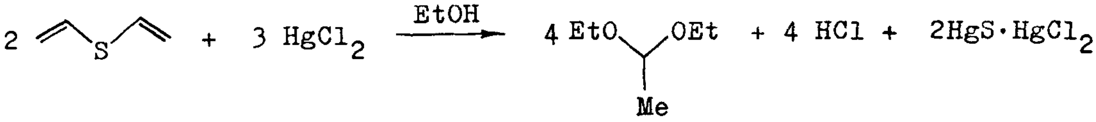
The addition of hydrogen halides and different acids to DVS has been described.[9,10,209–211] Hydrogen chloride[9,10,209] and hydrogen bromide add to DVS according to the Markovnikov rule to form di(1-haloethyl) sulfides.



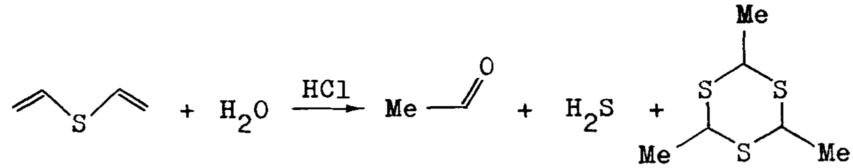
The addition of hydrogen halides to one double bond to form (1-haloethyl) vinyl sulfides is also possible.[10]



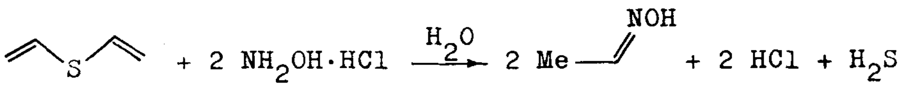
DVS in 20 % ethanolic $HgCl_2$ solution has been shown[212] to decompose quantitatively to afford acetaldehyde diethyl acetal, hydrochloric acid, and a complex mercury salt.



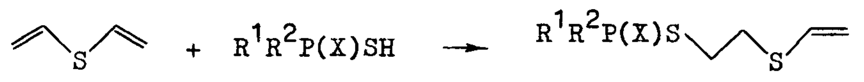
The hydrolysis of DVS with hydrochloric acid in aqueous dioxane leads to hydrogen sulfide, acetaldehyde, 2,4,6-trimethyl-1,3,5-trithiane, and a small amount of acetaldehyde and thioacetaldehyde oligomers.[212]



The same products are formed when DVS is hydrolyzed in an acidic solution of hydroxylamine hydrochloride, the acetaldehyde evolved being oximized.[212]

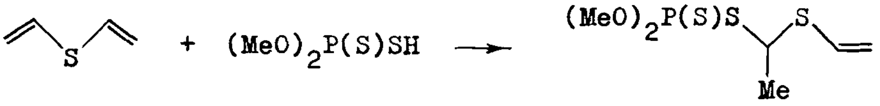


The extent of hydrolysis as determined by the amount of HCl and H_2S evolved is 62–68 % in the reaction with 6 % HCl and 80–85 % in the case of $NH_2OH{\cdot}HCl$.[212] There are known some patent data[210] concerning the addition of thiolo- and thionophosphoric acids to DVS. The reaction is performed in benzene, the acids are mixed with DVS in equimolar ratios. In this way, 2-vinylthioethyl esters of thiolo- and thionothiophosphoric acids as well as monoesters of phosphonic and phosphinic acids have been prepared and characterized.[210]

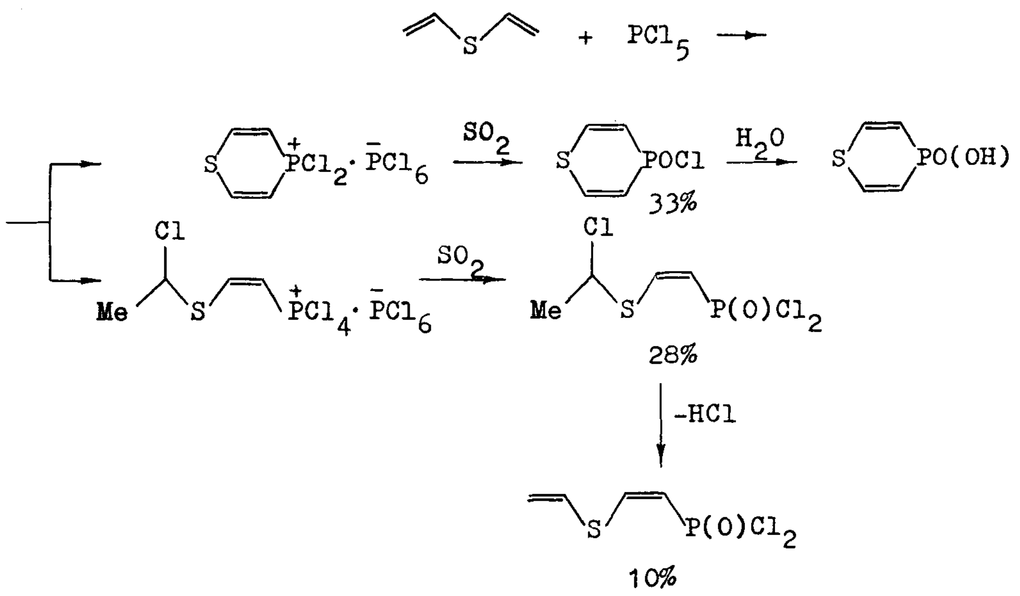


X = S, R^1 = R^2 = Me, Et, i-Pr, MeO, EtO; X = O, R^1 = R^2 = Me, EtO

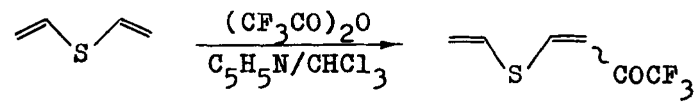
The yields range from 40 to 60 %. In the patent[210] these adducts were said without proof to have the "β-structure". Taking into account, however, the fairly high acidity of dialkyldithiophosphoric acids ($K_\alpha = 10^{-2}$) and the data of[211] concerning the interaction of dialkyldithiophosphoric acids with alkyl vinyl sulfides the reaction should be more reasonably considered to occur as an electrophilic addition *i.e.*, according to the Markovnikov rule, to yield "α-adducts". The adduct of dimethyl dithiophophoric acid to DVS has been shown, contrary to the patent claim,[210] to possess the "α-structure".[213]



This structure has unambiguously been proven by IR and ^{1}H NMR spectroscopy.[213] The addition of phosphorus pentachloride to DVS in benzene has been reported.[214] A high reactivity of the two DVS double bonds to phosphorus pentachloride has been shown. The reaction affords two different complexes of DVS with two PCl_5 molecules which, when decomposed with sulfur dioxide, give 4-chloro-4-oxo-2,5-diene-1,4-thiaphosphine and the acid dichlorides of β-(vinylthio)vinylphosphonic acid and β-(α-chloroethylthio)vinylphosphinic acid.



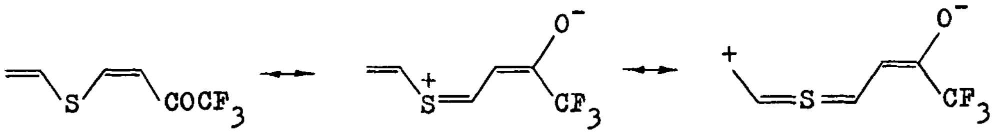
In vinylheteroatomic systems of the type $CH_2=CHX$- (X = O,S,N) the electrophilic β-substitution of hydrogen by a trifluoroacetyl cation usually proceeds smoothly.[215,216] With DVS, however, as evidenced from[217] only one vinyl group undergoes trifluoroacetylation.



cis : trans ≈ 1 : 2

The unexpected selectivity of the reaction indicates a qualitative change in the electronic nature of the vinylthio group under the effect of the 2-trifluoroacetylvinyl group and the involvement by the latter of an unshared electron pair of sulfur in a strong p-π-conjugation (stabilization of the unsubstituted double bond, destabilization of the corresponding cation).

The positive charge on the sulfur atom should favor the electron transfer to vacant orbitals, thus additionally decreasing the nucleophilicity of the vinylthio group.



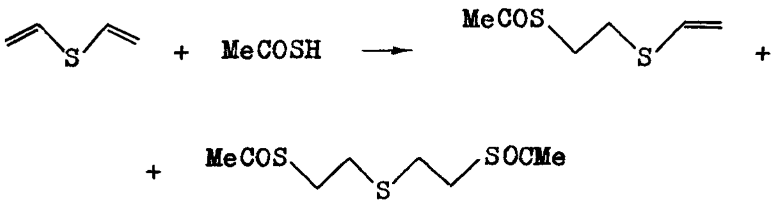
The structure of (2-trifluoroacetylvinyl) vinyl sulfide was ascertained by ^{1}H NMR, IR, and mass spectrometry.[217]

VII.3. Radical Addition

The additions of thioacetic acid[213] and mercaptans[213,218] to DVS are considered in this section. The conditions for selective addition of the above addends to only one vinyl group of DVS have been found. In this manner the corresponding functionally substituted vinyl sulfides have been synthesized.[213,218]

Thioacetic acid, being more reactive than simple mercaptans, may be efficiently used for the thiylation of multiple carbon—carbon bonds under both heterolytic and homolytic conditions.[219]

The reaction of thioacetic acid with DVS in an equimolar ratio proceeds exothermally to form the mono- and the diadduct (60 and 40 %, respectively).[213] The reaction's anti-Markovnikov course is supported by the ^{1}H NMR spectra of the compounds obtained. Thus, a homolytic addition occurs in this case.[213]



The methanolysis of di(2-acetylthioethyl) sulfide leading to 2,2′-dimercaptoethyl sulfide[220] provides additional evidence for the β-structure of the adduct.

Concentrated hydriodic acid in alcohol solution adds to DVS against the Markovnikov rule to form di(2-iodoethyl) sulfide.[209] Judged by the addition sense the process is a radical reaction.

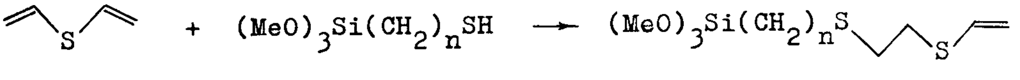
The homolytic addition of thiophenol to DVS affords di(2-phenylthioethyl) sulfide. The addition of mercaptans to DVS has been studied[213] in the presence of azobisisobutyronitrile and UV-irradiation or by thermal initiation alone (35–75 °C). The reaction leads to the mono- and the diadduct[213,218] in yields depending mainly on the reagent ratio. With *t*-butylmercaptan only the monoadduct was isolated:

R = Et, Pr, Bu, i-Bu, t-Bu

With three-fold excess of DVS the reaction can be directed towards predominant formation of 2-alkylthioethyl vinyl sulfides (up to 77 % yield). On the other hand even with a two-fold excess of mercaptan the diadducts are mainly formed (75–78 %). Azobisisobutyronitrile and UV irradiation increase the yield of oligomers. Therefore, the thiylation is better carried out by heating the reaction mixture to 60–70 °C for 3–6 hours. The chain length (from C_2 to C_4) of the mercaptan and branching in the β-position do not influence much the yield of monoadducts (64–77 %), whereas α-branching (t-C_4H_9), under the same conditions, sharply decreases the yield (34 %). The β-structures of the DVS thiylation products were proven by IR and ^1H NMR spectroscopy.

It has been suggested that 2-ethylthiomethyl-4-vinylthiothiacyclohexane is formed as a by-product[213] which is in agreement with [221] indicating the sensitivity of DVS to radical-initiated cyclopolymerization.

When extended to substituted mercaptans (trialkoxysilylalkanethiols)[218] homolytic thiylation of DVS affords in high yields 2-(trialkoxysilylalkylthio)ethyl vinyl sulfides, interesting organosilicon monomers and cross-linking agents.[218]

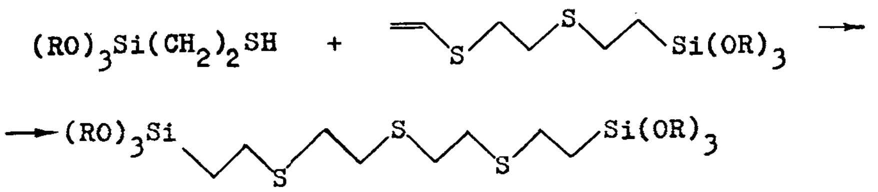


n = 1-3

The reaction proceeds smoothly upon thermal initiation (75–100 °C) with a mercaptan:DVS ratio of 1:3.

The catalysis with electrophilic reagents such as SO_2 also affords 2-(trialkoxysilylalkylthio)ethyl vinyl sulfides as the only reaction products which shows DVS to be very prone to homolytic processes.[218]

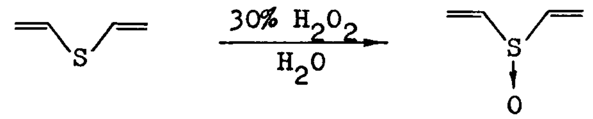
Unlike alkanethiols,[213] trialkoxysilylalkanethiols react with DVS to form mainly monoadducts. Diadducts can be identified only by ^1H NMR spectroscopy[218] in high-boiling fractions (10–20 % yield). It is not possible to isolate individual 2,2′-bis(trimethoxysilylalkylthio)diethyl sulfides even with two-fold excess of mercaptan over DVS. Under the latter conditions 30 % of the monoadduct and mainly an undistillable mixture which evidently consists of telomers and polyorganosiloxanes are formed. Thus, the addition of trialkoxysilylalkanethiols to DVS is rather hindered. This is supported by the fact that in a thermally initiated direct reaction of 2-(trimethoxysilylethylthio)ethyl vinyl sulfide and trimethoxysilylethanethiol the yield of 2,2′-bis(trimethoxysilylethylthio)diethyl sulfide does not exceed 40–45 %.



VII.4. Oxidation of Divinyl Sulfide

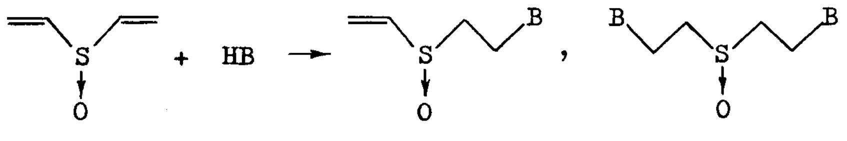
Divinyl sulfoxide has been prepared by oxidation of DVS with acetyl peroxide in diethyl ether solution.[222,223] The oxidation of di(2-phenylvinyl) sulfide with hydrogen peroxide affords di(2-phenylvinyl) sulfone.[74]

Only recently comprehensive studies of the oxidation of DVS with different oxidants have been undertaken[224–226] and the conditions[225,226] permitting an effective application for this purpose of dilute aqueous hydrogen peroxide instead of organic H_2O_2 solutions have been found.



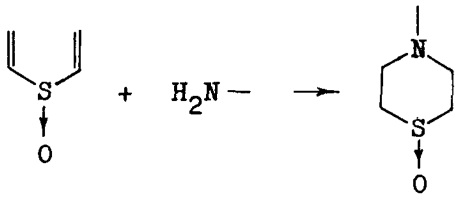
The reaction proceeds at 50–70 °C in the presence of emulsifiers (salts of higher carboxylic acids, alkylcellosolves, higher alkyl sulfates and sulfonates, polyacetals of various structure) with stoichiometric quantities of reagents.[226] The oxidation is selective with regard to divinyl sulfoxide (85 % yield); the product of further oxidation, divinyl sulfone, is not formed under these conditions.

The ready availability of the starting material and the safe and simple technology of the process are important prerequisites for making divinyl sulfoxide a large-tonnage

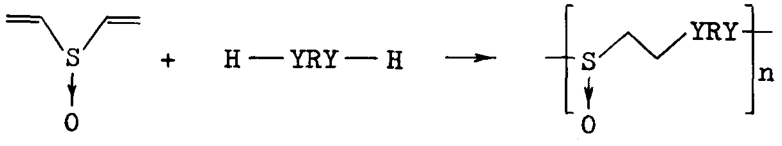


B = OR, SR, N< ; R = H, organic radical

product. The chemistry of divinyl sulfoxide is developing rapidly.[227–242] Divinyl sulfoxide opens up previously 'forbidden' routes to substituted sulfoxides of diverse structure, including substituted vinyl sulfoxides,[227–230,238–240] and to little-known heterocycles of the tetrahydro-1,4-thiazine-1-oxide type.[231–233]



Important possibilities for producing basically new polymers by polyaddition to divinyl sulfoxide of various bifunctional addends such as glycols, diamines, and dithiols are being recognized.[234–236,241]

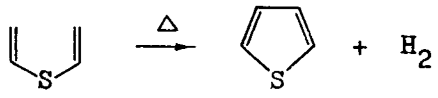


Y = O, S, N; R = organic unit

Interesting physiologically active substances have already been found among divinyl sulfoxide derivatives.[237]

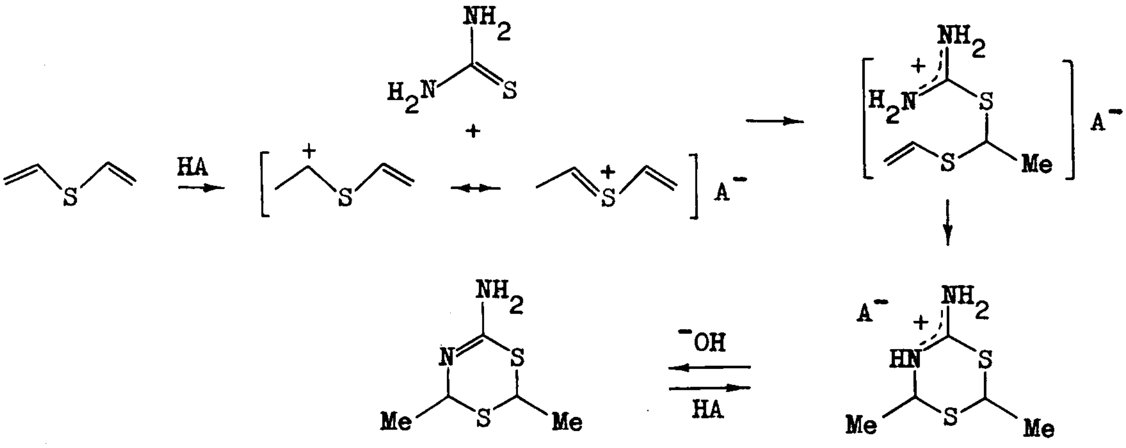
VII.5. Cyclization Reactions

At 450–560 °C DVS undergoes dehydrocyclization to form thiophene.[243]



The reaction is carried out in a flow system (an empty quartz tube) under nitrogen. The conversion of DVS at 560 °C (feed rate of DVS is 10 ml/h, that of nitrogen 3 l/h) is 95 %, the maximum yield of thiophene, however, does not exceed 40 % due to strong resinification. Along with thiophene, a mixture of low-boiling unidentified products of DVS pyrolysis (10–15 % of the condensate mass) is formed. Presence of hydrogen sulfide does not increase the yield of thiophene. Numerous possibilities for the synthesis of heterocyclic systems directly from DVS are still far from being fully exploited. For this purpose one can freely use electrophilic and/or radical addition of different bifunctional addends as well as hydrosilylation with dihydrosilanes or hydrodisiloxanes. Along with an extremely easy synthesis of 1,4-dithiane from DVS and hydrogen sulfide, syntheses of diverse macroheterocycles (including crown-like ones) by addition of diols and dithiols to DVS under high dilution and in the presence of metal cations (creating a template effect) are also thought to be within easy reach.

It has been found recently[244,245] that cycloaddition of thiourea to DVS results in new heterocyclic systems. The cycloaddition proceeds smoothly in the presence of strong acid to lead to 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine salts.



A = Cl, Br, ClO_4, NO_3, 4-Me-$C_6H_4SO_3$

These salts are obtained by mixing the reagents in equimolar quantities (or with slight excess of DVS) in water or alcohol at 40–50 °C (in 70–90 % yield). Use of alcohol instead of water as the solvent produces a homogenous medium thus increasing the yield by 10–20 %.

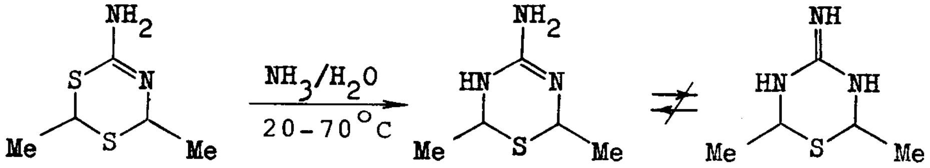
The cycloaddition only proceeds in the presence of acids. The reaction course is greatly affected by the nature of these acids. With acetic, trifluoroacetic, and dimethyldithiophosphoric acid no cycloadducts can be obtained.[244,245] This dependence of the reaction pathway on the acid strength shows that the cyclization starts with protonation of the DVS double bond to form a mesomeric carbonium-sulfonium cation which is trapped by the thiourea molecule. Subsequent protonation of a second double bond of the intermediate is followed by ring closure. The initiation of the reaction according to this scheme may be triggered by equilibrium concentrations of a strong acid present in the reaction mixture due to dissociation of the isothiouronium salt.

Introduction of an electron-withdrawing substituent into the DVS molecule disfavors this suggested protophilic cyclization. Thus, under the same conditions di(2-phenylvinyl) sulfide fails to react with thiourea and displays only a change in the isomer ratio.

Together with their loss of protophilicity the oxidized DVS derivatives (divinyl sulfoxide and divinyl sulfone) lose the ability for cycloaddition. Instead of the cycloaddition products linear diadducts are formed by nucleophilic addition.[245]

2*H*,6*H*-2,6-Dimethyl-4-amino-1,3,5-dithiazine salts, when treated with alkali, can give the free dithiazine which again forms salts with aqueous acid solutions. In this way it is possible to obtain salts which cannot be prepared by direct interaction of DVS with thiourea.[245] The synthesis of various 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine salts by exchange with another salt is also possible.

Treatment of 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine or its salt (the nitrate, for example) with 20–25 % aqueous ammonia at 20–70 °C leads to ready selective exchange of one of the sulfur atoms for a nitrogen atom to give a new heterocyclic system, 2*H*-2,6-dimethyl-4-amino-3,6-dihydro-1,3,5-thiadiazine in 62–88 % yield.[246]



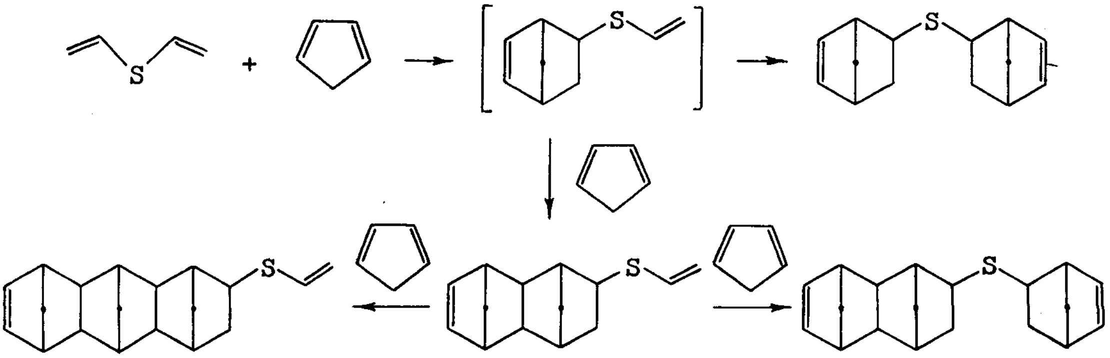
The analysis of the ^{1}H NMR spectra of 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine, its acyl derivatives, and 2*H*-2,6-dimethyl-4-3,6-dihydro,amino-1,3,5-thiadiazine, recorded in different solvents and using lanthanoid shift reagents, has shown[247] these compounds to exist in the amino form. As far as the isomer composition of these compounds is concerned, one may suggest, although the spectra are less informative in this respect, a *cis*-arrangement of the methyl groups relative to the ring plane.

These results are confirmed by inspection of the IR spectra of 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine and its 4-dideuteroamino derivative[248] (deuteration degree 70–75 %) both in solutions (CCl_4, $CHCl_3$) and in the crystalline state.

From a study of the basic properties of 2*H*,6*H*-2,6-dimethyl-4-amino-1,3,5-dithiazine and its *N*-acyl derivatives the conclusion has been drawn that the *N*-acyldithiazines in methanol and acetone solution exist presumably in the amino form independently of the nature of the acyl group.[249]

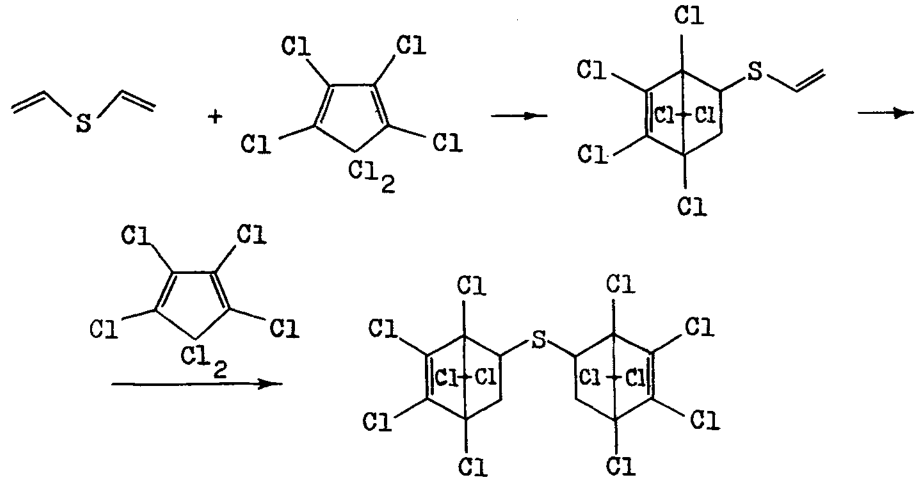
VII.6. Diels-Alder Reactions

Only few investigations of the Diels-Alder synthesis involving vinyl sulfides and sulfones are known.[223,250–253] DVS has been treated with cyclopentadiene at 180 °C.[222] The homopolymerization was inhibited by excess cyclopentadiene and phenyl-α-naphthylamine.[222]

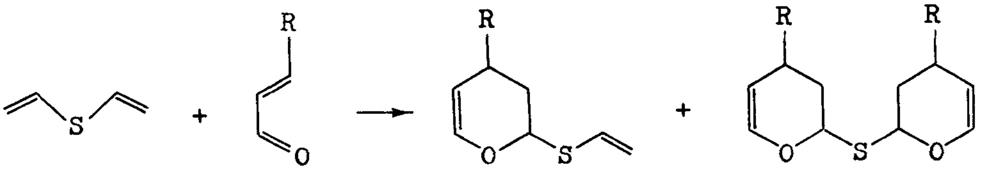


Under these conditions no monoadduct was found, di- and triadducts being the main reaction products.[222]

The reaction of cyclopentadiene with divinyl sulfoxide and divinyl sulfone has also been carried out. The reactivity decreases in the following order: divinyl sulfone > divinyl sulfoxide > DVS.[222] When hexachlorocyclopentadiene is used as the diene the reactivity of this series reverses.[254] DVS reacts nearly quantitatively with hexachlorocyclopentadiene to form 1,4,5,6,7,7-hexachloro-2-vinylthiobicyclo[2.2.1]-5-heptene and 2,2-bis(1,4,5,6,7,7)hexachlorobicyclo[2.2.1]-5-heptenyl sulfide.[254]



The reaction affords almost exclusively the *endo*-form.[254] The reaction of DVS with α,β-unsaturated aldehydes has been studied.[255] Depending on the reaction conditions mono- or diadducts are formed.

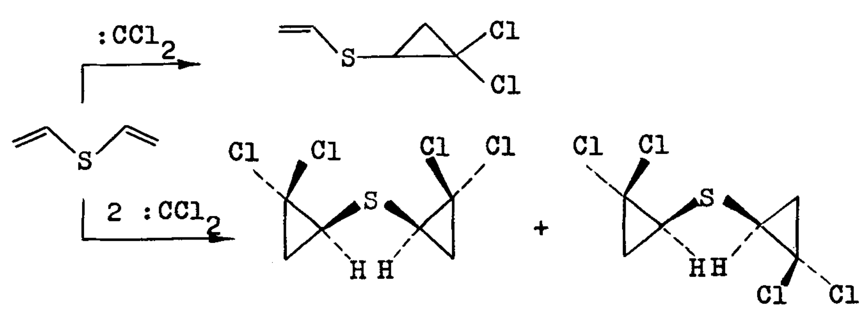


R = H, Me

The yields of 2-vinylthio-3,4-dihydropyrane, 2-vinylthio-4-methyl-3,4-dihydropyrane (isomer ratio 95:5), and bis(3,4-dihydropyran-3-yl) sulfide are 47, 17 and 49 %, respectively.[255]

VII.7. Reactions with Carbenes

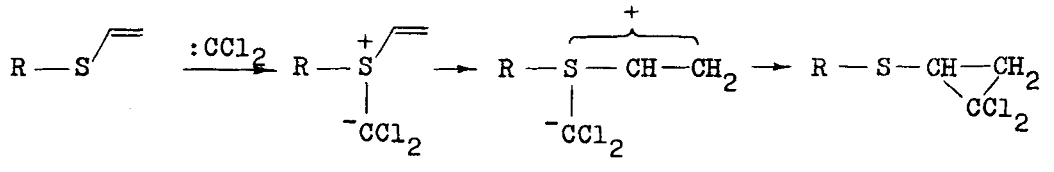
The addition of dichlorocarbene to DVS in a two-phase system has briefly been reported[256] (no physical data and adduct yields are given).



The reaction of DVS and dichlorocarbene obtained from chloroform and potassium *t*-butoxide leads to 2,2-dichloro-1-vinylthiocyclopropane (40 % yield) and bis(2,2-dichlorocyclopropyl) sulfides (5 % yield, *meso-d,l* mixture 1 : 1).[257,258] Dibromocarbene generated under the conditions of phase transfer catalysis adds to DVS to form 2,2-dibromo-1-vinylthiocyclopropane in 30 % yield.[258]

For a mechanistic elucidation of the addition of dichlorocarbene to the vinylthio group the relative-rate constants, k_{rel}, for a series of vinyl sulfides, including DVS, have been measured.[257,258]

The rate of the dichlorocarbene addition to vinyl sulfides is 5–6 times as high as that to vinyl ethers; thus, k_{rel} for DVS is 2.9 ± 0.3 whereas for divinyl ether this value is 0.6 ± 0.1.[258] With vinyl sulfides and vinyl ethers the reaction rates are quite differently affected by steric factor: in the case of vinyl sulfides reaction rate drops[†] whereas with vinyl ethers it increases.[258] This is due to the fact that dichlorocarbene in the reaction with vinyl sulfides reacts with the sulfur atom rather than with the double bond to form an ylide which further rearranges to a dipolar ion to give the cyclopropane.[258]

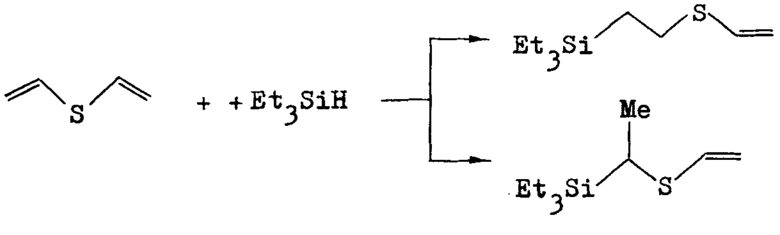


R = Me, Bu, i-Bu, t-Bu, Ph, CH=CH$_2$

The reaction of vinyl sulfides with carbenes is orbital controlled.[258]

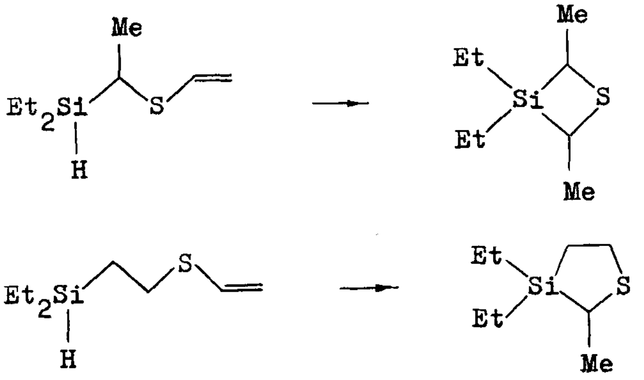
VII.8. *Hydrosilylation*

Regardless of a patent[259] claiming the hydrosilylation of vinyl sulfides in the presence of platinum catalysts to be impossible, the addition of the silyl group proceeds in both α- and β-position of DVS.



In the addition to DVS, hydrosilanes form, along with α- and β-monoadducts, 1-thia-3-silacyclobutanes and 1-thia-3-silacyclopentanes.[262–264]

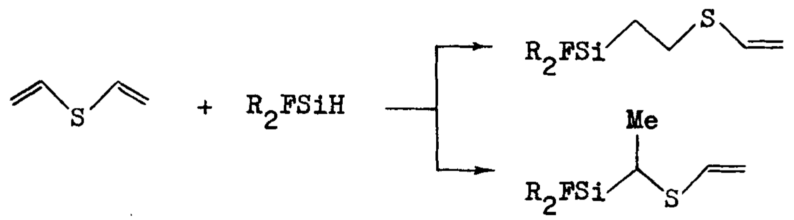
[†] With growing size of the alkyl group.



The formation of these heterocycles is explained[262,264] by intramolecular hydrosilylation of the monoadducts.

The hydrosilylation of DVS in the presence of H_2PtCl_6 and $(Ph_3P)_3RhCl$ is unselective to give predominantly the monoadduct of β-structure, *i.e.*, according to Farmer's rule.[261,265–267] The process is complicated by a number of side-reactions including cleavage of the C—S bond with hydrosilane as the major one.[261,265]

In the case of DVS hydrosilylation with dialkylfluorosilanes[268] in the presence of H_2PtCl_6, the addition according to Farmer's rule is the prevailing route as well.

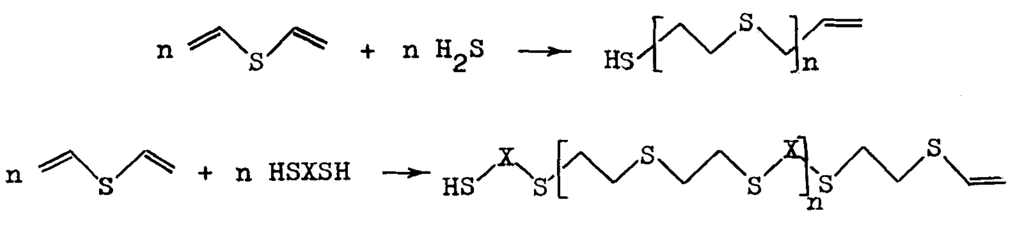


R = Me, Et, Pr

The yield of the monoadducts is 35–50 %. Along with the monoadducts, diadducts are formed.[268]

VII.9. *Polyaddition of Hydrogen Sulfide to Divinyl Sulfide*

As we have shown previously, polyalkylene sulfides of the type described in[269] and their heteroatomic analogs can be obtained by reaction of DVS with hydrogen sulfide and dithiols.

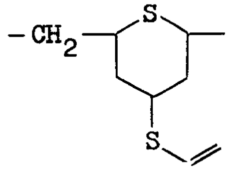


$X = (CH_2)_2,\ (CH_2)_2(OCH_2CH_2)_3$

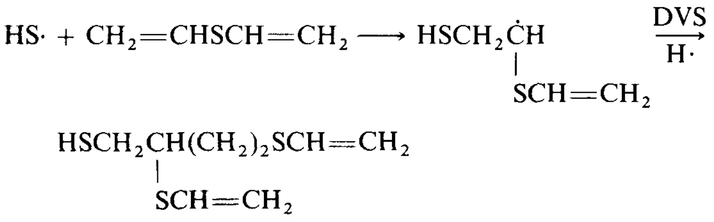
The polyaddition follows a free-radical mechanism without either catalysts or solvents at 40–55 °C. The yield of polyalkylene sulfides is 70–98 %. As a rule, these are white powders of poor solubility in conventional organic solvents, with a melting temperature within the 158–175 °C range. The decomposition starts at a temperature beyond 200 °C. The sulfur content is 45–56 %. In the case of polyaddition of hydrogen sulfide to DVS the polyethylene sulfide formed contains up to 40 % of an ether soluble, waxy fraction.

The present reaction allows one to synthesize polyalkenyl sulfides with regularly alternating ethylene sulfide (CH_2CH_2S) and polyalkylene or polyheteroalkylene sulfide units. These polymers possess reactive vinylthio and thiol groups as terminals.

Taking into consideration that DVS is prone to cyclopolymerization[221] it is safe to assume that the polyalkylene sulfides formed contain, at least to some extent, cyclic structures of the type:

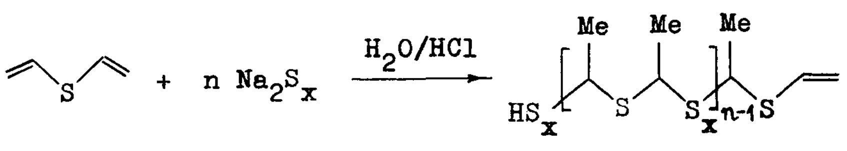


Insoluble fractions of polyadducts seem to be formed due to chain branching according to the following scheme:



$$HS\cdot + CH_2{=}CHSCH{=}CH_2 \longrightarrow HSCH_2\underset{\displaystyle SCH{=}CH_2}{\dot{C}H} \xrightarrow[H\cdot]{DVS} HSCH_2\underset{\displaystyle SCH{=}CH_2}{CH}(CH_2)_2SCH{=}CH_2$$

With hydrogen polysulfides (sulfanes) DVS gives liquid polysulfide oligomers, thiokols of a new type with terminal vinylthio groups, which appears rather promising for curing and modification.

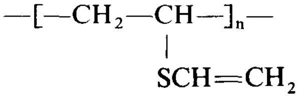


x = 1-4, n = 3-7

Such thiokols are obtained by reaction of DVS with hydrogen polysulfides formed directly in the reaction medium from sodium polysulfide and hydrochloric acid. Depending on the DVS-hydrogen polysulfide ratio and the sulfur content of the latter, one can prepare thiokols of varying consistency, the sulfur content ranging from 60 to 75 %.

VII.10. Radical Homopolymerization

In 1959 Scott and Price reported[15] that the free-radical ploymerization of DVS to 50 % conversion gives completely soluble polymers which were assigned the usual structure:



$$\text{—[—}CH_2\text{—}\underset{\underset{SCH=CH_2}{|}}{CH}\text{—]}_n\text{—}$$

The fact that the remaining vinyl groups do not polymerize further to form a cross-linked polymer points to a lower reactivity of these isolated double bonds compared to the double bonds of the monomer which are, in the authors' opinion, mutually activated through conjugation.[15]

However, taking into account more recent reports[270-274] of ready polymerization of unconjugated alkyl vinyl sulfides (including branched ones) upon radical initiation, the above explanation can no longer be considered as acceptable.

The oxygen analog of DVS, divinyl ether, is known[275,276] to undergo free-radical induced cyclopolymerization involving the two double bonds.

As was shown later,[277,278] the divinyl ether polymers thus obtained mainly consist of saturated bicyclic units and, to a lesser extent, of monocyclic units with vinyloxy substituents.

Bearing in mind these data, as well as the fact that the molecular geometry[205] and the charge density distribution[279] are rather similar in DVS and divinyl ether, one can find it quite difficult to explain the fundamental difference in the structure of polymers of these compounds (assuming[270] that DVS is polymerized with the participation of only one double bond). These considerations guided a group of Italian scientists[221] in their detailed study of the structure of polydivinyl sulfide obtained under radical conditions. In their opinion, the solubility of the polymer is more dependent upon the small number of remaining double bonds than the low reactivity of the latter.[221] They performed the polymerization of DVS both in block and in benzene solution at 60 °C using azobisisobutyronitrile as the initiator ($1.56 \cdot 10^{-2}$ mole/l). The monomer conversion never exceeded 5 %. The polymer completely dissolved in benzene, CCl_4, $CHCl_3$, CH_2Cl_2, and CS_2 and was reasonably stable when exposed to direct light and atmosphere. The remaining double bonds in the polymer were determined by IR spectroscopy from the 1584 cm^{-1} band peak intensity ($CH_2{=}CHS$).

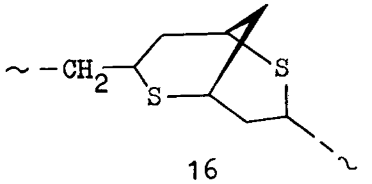
The double-bond content of the polymer decreases with decreasing monomer concentration in the solution,[221] but even in the block polymer only 0.28 vinyl groups are present per elementary unit, *i.e.*, there is one double bond per 3-4 DVS molecules which underwent polymerization.

All this is common in unconjugated diene cyclopolymerization.[280] Consequently, there is every reason to attribute the radical polymerization of DVS to a process of this type, especially to a process similar to the bicyclic cyclopolymerization of divinyl ether. In any event, the formation of highly strained four-membered rings according to the scheme:

is definitely excluded since the UV spectra of the polymers display no absorption at 275 nm characteristic of thietanes.[281]

Having compared the number of remaining double bonds in polymers of DVS and divinyl ether, the authors[221] have concluded that, for a given monomer concentration, the DVS polymer contains more cyclic units than the divinyl ether polymer. Thus, the radicals formed from DVS are more prone to cyclization.

This is the natural result of a lower reactivity of the DVS radicals due to their higher resonance stabilization caused by interaction of the unshared electron with the neighboring sulfur atom. The resonance parameter Q for DVS and divinyl ether is 0.58 and 0.037, respectively.[280] The data regarding the free-radical polymerization of DVS and divinyl ether are in agreement with the hypothesis that intramolecular macroradical reactions become more favorable when the rate of the propagation step decreases. Using an equation[278] relating the residual number of vinyl groups in the polymer with the monomer concentration and the rate constants of the most probable cyclization reactions, the authors[221] conclude that the DVS polymers consist mainly of bicyclic (**16** and **17**) and, to a lesser extent, monocyclic structural units (**18** and **19**).



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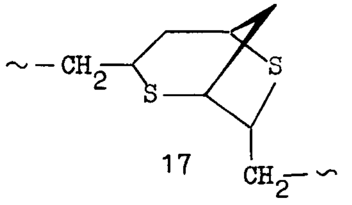

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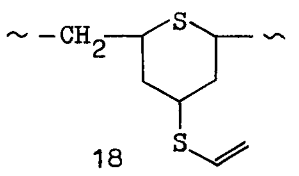

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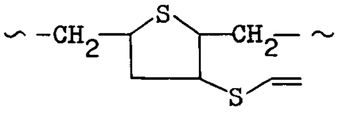
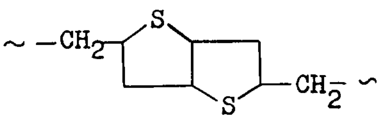
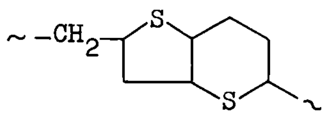
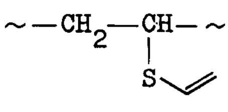


19

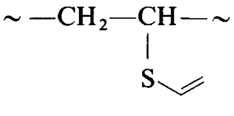
The structural units shown below, including linear blocks, are practically absent in the polymers.







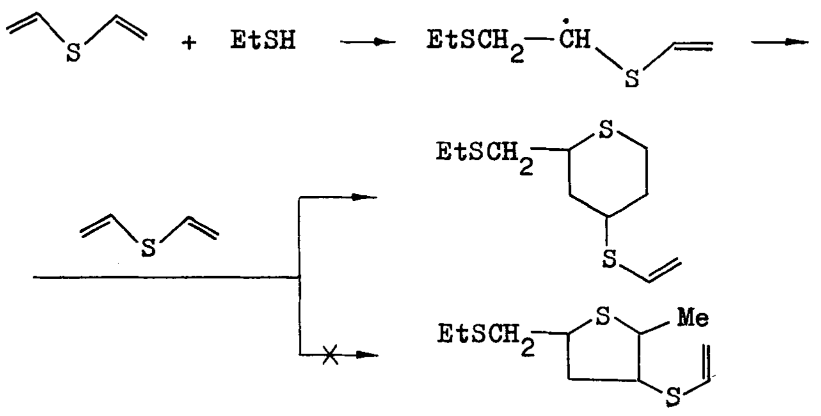
The authors[221] come to the conclusion that the linear structure suggested



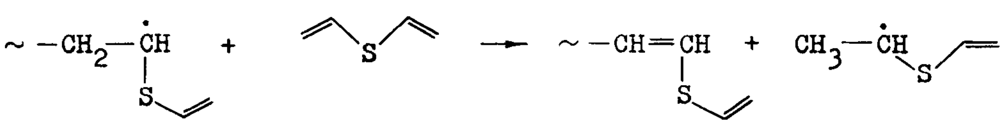
$$\sim\!-CH_2-\underset{\underset{S\diagdown\!\!\diagup\!\!\!=}{|}}{CH}-\!\sim$$

previously[280] for the DVS polymers is totally unrealistic.

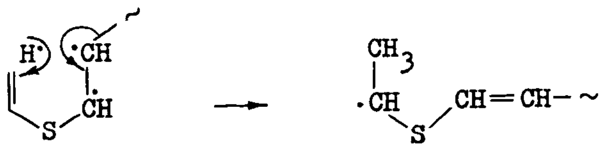
The conclusion regarding the predominant formation of six-membered rings during the radical polymerization of DVS is supported by identification of 2-(ethylthiomethyl)-4-(vinylthio)thiane in products of the homolytic addition of ethanethiol to DVS.[213] The isomer with a five-membered ring, 2-methyl-3-(vinylthio)-5-(ethylthiomethyl)thiolane has not been observed.



It should be noted, however, that the residual double bonds in the DVS polymer may belong to not only the side-chain vinylthio groups, but also to the CH=CHS fragments built into the macromolecule through a chain-monomer transfer reaction.



An intramolecular concerted electron transfer in the 6-membered intermediate involving hydrogen atom migration is also possible (the curved arrows denote the homolytic scission of a C—H bond):



In these two cases a less active disubstituted ethylene fragment should be formed. Since the authors' estimations[221] are based on the residual unsaturation of the polymers which is completely attributed to side-chain vinylthio groups, the above chain-transfer processes cannot but affect the correctness of their conclusions.

The IR spectrum of the polydivinyl sulfide obtained in the presence of azobisisobutyronitrile at 70 °C displays broad bands in the 1620–1640 cm^{-1} region, assigned[282] to partial structures of the type $SCH_2CH{=}CHCH_2S$. In the ^1H NMR spectrum the olefinic protons of this unit must be assigned, in the authors' opinion,[282] to the singlet in the 5.4–5.7 ppm range. The intensity of this signal increases upon heating of the polymer

(180–200 °C) whereas the intensity of the $CH_2{=}CHS$ proton signals decreases simultaneously. If the above fragments are, in fact, contained in the DVS polymer, it remains quite uncertain in which way they are formed.

A cross-linked granular polymer has been obtained[283] by DVS polymerization initiated with azobisisobutyronitrile (1.5–10 %) in an aqueous emulsion containing starch and sodium nitrite in amounts of 4–20 % of the monomer mass (60–90 °C, 24–28 h). Under these conditions polydivinyl sulfide is formed as spheric, light-brown granules in a yield of over 90 %.

VII.11. Radical Copolymerization

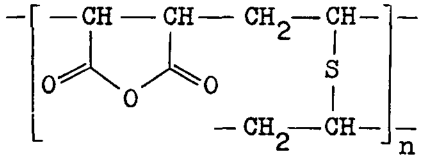
As early as 1944 the preparation of DVS copolymers with butadiene in water emulsion was reported.[284] The copolymers were prepared in an effort to substitute natural rubber.

In a patent[285] DVS was mentioned among numerous other cross-linking agents used for the preparation of macroreticular copolymers in the presence of water as a porophore. The main monomers mentioned in the patent are acrylic and metacrylic acids, various acrylates and metacrylates, styrene, vinyltoluene, vinylnaphthalene, substituted 3- and 4-vinylpyridines, 7-methyl-4-vinylquinoline, 1- and 3-methyl-5-vinylisoquinoline, *N*-vinyllactams, etc. (about 40 altogether). However, the patent specification gives neither concrete examples of DVS copolymerization nor characteristics of the DVS copolymers.

The technology[285] provides for the preparation of cross-linked block copolymers which impedes subsequent introduction of functional groups into the polymer matrix and further exploitation of the final product, an ion-exchange resin.

According to patent data,[286] DVS copolymerizes with acrylonitrile at room temperature without initiator. Thus, the DVS/acrylonitrile mixture (7 : 3 by weight), allowed to stand at room temperature, after 4 hours acquires the appearance and consistency of milk, 12 hours later it becomes a gel-like mass and after 108 hours followed by 20 hours heating at 100 °C a solid (23.7 % sulfur content) is formed. Analogously, copolymers of various sulfur content are obtained, depending on the composition of the starting mixture. Methyl acrylate and DVS (19 : 1 by weight) in the presence of 0.02 % benzoyl peroxide afford a solid of 2.58 % sulfur content.[286] Similar products were obtained by copolymerization of DVS with vinyl acetate, styrene, ethyl and butyl acrylate, and methacrylonitrile.[286] The copolymers can be used for manufacturing shaped items, coatings, varnishes, adhesives, putties, insulators, interlayers for laminated plastics, etc.[286]

Three-dimensional DVS/maleic anhydride (MA) copolymers containing 11–22 % of sulfur have been tested as gold sorbents.[287–290]



They are obtained in high yield (80 %) in the presence of radical initiators or by thermal copolymerization.

For the synthesis of these polymers the monomer mixture compositions were varied in a wide range. With mixtures containing 50–75 moles % of MA the copolymers obtained were of nearly constant composition (1.5 mole of MA per 1 mole of DVS). In this case, the swelling degree α, of the copolymers in acetone does not exceed 100 weight %. With excess DVS the copolymers are richer in this monomer (the amount of sulfur can reach 30 %). They swell considerably in acetone (α = 350 %) which may be explained by the presence of cyclic blocks of DVS units in the copolymer structure. The exchange capacity of the copolymers for the sorption of gold from hydrochloric acid solutions is 9.5–11.2 %.[290] The highest exchange capacity is observed in the copolymers containing 14–16 % of sulfur. Thus, the copolymer with 16 % S content takes up 98.2 % of gold from 42 % hydrochloric acid solution, its total exchange capacity being 112.5 mg/g (whereas that of the well-known AP-2 sorbent made from styrene-divinylbenzene resin is 25 mg/g or 2.5 % in the same solutions[287,290]). In the sorption of gold from technological solutions the copolymer exchange capacity is 135 mg/g or 13.5 %.[290]

It is valuable that upon the absorption of gold from both rich and poor solutions the exchange capacity is practically constant. Thus, upon the sorption of gold from 3.8 % solution the copolymer capacity is within the 95–100 mg/g range. The gold is eluted from the sorbent with thiourea sulfate solution without changing the sorption properties of the copolymer. The same copolymers can selectively recover gold from cyanide and thiourea solutions.[290]

High capacity and selectivity of the three-dimensional DVS/MA polymer for gold and palladium recovered from chloride and sulfate solutions containing platinum, osmium, and large quantities of base metals have been reported.[289] Thus, the static capacity of the copolymer for gold and palladium in 3 N hydrochloric acid is 175 and 75 mg/g, respectively; that in 3 N sulfuric acid is 91 and 100 mg/g.

The capacity of cation exchangers obtained from DVS/MA copolymers is 7–9 mg-eqv/g (for 0.1 *N* NaOH).[288]

The measurement of the molecular-mass distribution of polymers and other tasks of gel-chromatography require a wide range of gels different in both chemical composition and physical structure. The cross-linked DVS/MA copolymer has also been suggested as an organophilic gel.[288]

The higher and readily variable swelling of cross-linked DVS copolymers opens great possibilities for their application in gel-penetrating chromatography.[288]

The ternary-copolymerization of DVS/MA/vinyl phenyl ether[288] allows copolymers of even higher swelling (to 1100 mass %) to be prepared. The synthesis of ternary copolymers is carried out[288] in the presence of a radical initiator (azobisisobutyronitrile).

At the present time the area of practical application of DVS has already been delineated rather definitely. This is the synthesis of ion-exchange resins and complexing sorbents. The synthesis of sulfur-containing ion exchange resins and sorbents from styrene, methyl acrylate, acrylonitrile, vinylpyridine, 2-methyl-5-vinylpyridine and *N,N*'-diphenylmethane-bis-maleimide has been achieved[169,170,291] by cross-linking the polymer backbone with DVS. The resinous structure of the copolymer, which is mainly dependent upon the specificity of the DVS/vinyl monomer copolymerization increases the swelling, ion-exchange capacity, and kinetic properties as well as the mechanical strength (95–100 %) and osmotic stability of these new ion exchangers.[291,292]

The mechanical strength and osmotic stability are defined as the percentage of the sorbent granular mass remaining intact after ball-milling and multiple treatment with solvents, respectively.

In comparison with their divinylbenzene analogs, these polymers display higher permeability for large organic molecules (dyes, antibiotics, enzymes), osmotic stability, and mechanical strength. The presence of sulfide sulfur atoms ('mild', readily polarizable, basic and complexation sites) in the copolymer matrix imparts the ion exchangers a highly selective complexing affinity with respect to metals of variable valency and to the platinum group metals. Sulfur-containing ion-exchange resins can be used for the selective recovery and separation of metals such as copper, nickel, cobalt, tungsten, molybdenum, mercury, lead, gold, silver, and platinum-group metals from industrial solutions and waste water. The sulfur-containing sorbents, such as DVS/vinylpyridine copolymers, for example, possess ion-exchange properties and can remove halogen ions from aqueous solutions. In contrast to, for example, carboxyl group-containing cation exchangers, sulfur-containing ion exchangers are able to take up metal ions from organic solvents.[291]

At present, over 30 new types of sulfur-containing anion, cation, and ampholytic ion exchange resins and sorbents with various functional groups have been obtained.[291,292]

Styrene/DVS copolymers with high mechanical strength (to 99.5 %), osmotic stability (to 99.6 %), and sorption capacity for copper (90.3 mg/g from an acetone solution of copper bromide containing 0.5 g/l of copper) have been obtained[291] in the presence of azobisisobutyronitrile (in a ratio of 0.046–0.140 mole DVS per mole of styrene). Sequential treatment of the above copolymer with monochlorodimethyl ether (8–20 parts by weight) in the presence of zinc chloride and aqueous trimethylamine (10–20 parts by weight) leads[291] to highly basic anion exchange resins useful in the highly efficient purification of fungous lipase culture solutions affording ultrapure crystalline enzyme (yield 97.5 %). The activity of the purified enzyme is 5.5 times as high as that of the starting enzyme.

Modification of the styrene/DVS copolymer with monochlorodimethyl ether in the presence of ferric oxide followed by treatment with a 1:3 mixture of DMF and 20 % aqueous alkali solution (2–6 parts by weight per 1 part of the copolymer) affords[291] a weakly basic anion exchanger exhibiting selective sorption for gold and silver (34.2 mg/g and 21.2 mg/g, respectively) from solutions containing 16.35 mg/l of gold and 43.0 mg/l of silver.

The above modified copolymer is treated with 98 % sulfuric acid (10 parts by weight per 1 part of the copolymer) at 100 °C for 4 hours in order to obtain a "sulfocationite"[291] used for the recovery of yeast cells from culture solutions (the sorption capacity for yeast cells is 47.3 mg/g).

The copolymerization of DVS with methyl acrylate in a 0.014–0.124:1 ratio in the presence of azobisisobutyronitrile followed by treatment of the copolymer with aqueous alkali leads to a carboxyl group-containing cation exchange resin displaying high osmotic stability, mechanical strength, and high exchange capacity for streptomycin from industrial solutions (7.45 mg-eqv/g).[291]

Treatment of the copolymer with 15–20 % aqueous aliphatic amine allows a cation exchanger with a high selective exchange capacity for lysine (1 g/g) to be prepared.[291]

When the copolymer is treated with anhydrous aliphatic amine a weakly basic anion exchanger possessing exchange capacity for molybdenum (from industrial molybdenum nitrate solutions) of 540.1 mg/g is obtained.[291] If this procedure is followed by treatment of the copolymer with sodium chloroacetate, an amphoteric ion exchanger with a high capacity for the uptake of nickel (320 mg/g) from nickel sulfate solutions is formed.[291]

A carboxyl group containing cation exchanger with a high capacity for the uptake of copper ions from acid (68.1 g/l) and ammonia-carbonate (67.6 g/l) solutions has been obtained by subsequent treatment of the copolymer with a DVS/methyl acrylate mixture in the presence of azobisisobutyronitrile followed by copolymerization in emulsion and treatment with 10-fold excess of 25 % aqueous alkali. The cation exchanger exhibits excellent kinetic properties: the full saturation of the sample with copper takes ten minutes. The osmotic stability of the cation exchanger is 100 %. Repeated sorption-desorption processes can be carried out without deterioration of the technological properties of the ion exchanger.[237]

A water soluble polyelectrolyte made from an acrylic acid copolymer and DVS is used as a drilling fluid stabilizer.[293] Drilling fluids with an added stabilizer acquire higher stability and decreased water recoil.

The polyfunctional copolymer from 2-methyl-5-vinylpyridine cross-linked with divinylbenzene and DVS (the "snake-in-cage" type) is highly selective for the platinum group metals (Pt, Pd, Ru, and Rh). It efficiently separates platinum group metals from a mixture containing Cu^{2+}, Fe^{2+}, Fe^{3+}, Ag^{+}, and platinum group metals in a 500 : 1 ratio. The degree of desorption of platinum group metals from the sorbent reaches 92–97 %.[237]

The vinylpyridine/DVS copolymer displays a high sorption capacity for platinum group metals (46.2 mg/g) from solutions containing $1.5 \cdot 10^{-6}$ g/l of these metals. The mechanical strength and osmotic stability of the sorbent is 99.7 and 99.8 %, respectively.[291]

The copolymerization of DVS with acrylonitrile in a 0.11–0.6 : 1 ratio in the presence of azobisisobutyronitrile followed by treatment with 25 % aqueous alkali solution affords a carboxylic group containing cation exchanger with high osmotic stability and exchange capacity for cadmium (83.6 mg/g) from ammonia-carbonate solutions.[291]

A weakly basic anion exchanger has been prepared by treatment of the above copolymer with ethylenediamine or hydroxylamine. The anion exchanger is highly specific for the chloride ions.[291]

The radical copolymerization of DVS with methylmethacrylate, styrene, and acrylonitrile has been studied by sol-gel analysis of the copolymerization products obtained both in bulk and in solutions.[294] The swelling degree of copolymers of DVS with vinyl monomers has been shown to increase in the following order: acrylonitrile < styrene < methyl methacrylate. Thus, for example, a DVS/methyl methacrylate copolymer with a 1900 % swelling degree in benzene has been obtained.[294]

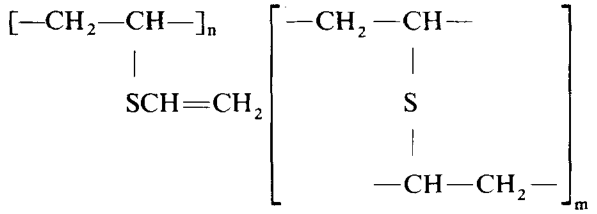
The above information, although held in rather general terms, shows that the ion exchange resins and sorbents synthesized with DVS as the cross-linking agent possess a number of unique properties and are, in many respects, superior to the ion exchangers applied in industry at present. The possibilities of practical application of ion exchange resins from DVS are far from exhausted.

The results obtained with DVS copolymers in other fields also look rather promising. Thus, the possibility of using DVS as a cross-linking agent in the synthesis of new rubbers has been shown in the case of acrylate and butadiene-nitrile rubbers.

VII.12. Cationic Polymerization and Copolymerization of Divinyl Sulfide

According to patent data[295] DVS rapidly polymerizes in the presence of $AlCl_3$ or gaseous BF_3 in methyl chloride or pentane. The copolymerization of DVS with isobutylene, cyclohexene, and 1-hexadecene is also claimed in this patent. Thus, when treated with $AlCl_3$ (2–3 %) in CH_3Cl at -24 °C for 5.5 hours, DVS and isobutylene (1:10) afford a white, granular, non-melting copolymer containing 15.2 % of sulfur. The copolymer has a poor solubility in benzene. Increasing the isobutylene content one can obtain liquid copolymers.[295] DVS and cyclohexene (1:19 by mass) in the presence of 6 % of $AlCl_3$ at 70 °C for 14 hours form a yellow granular product, insoluble in alcohol and ether and containing 28.1 % of sulfur (no yield reported). DVS and 1-hexadecene (1:19 by mass) when being mixed with 6 % of $AlCl_3$ for three weeks give a mixture of liquid and solid copolymer, the latter contains 17.2 % of sulfur and is insoluble in ether. Solid DVS copolymers have been suggested for manufacturing oil-resistant sealings, glands, hermetics, etc.[295] Liquid copolymers can be used as rubber softeners.[295]

DVS polymerization in the presence of cationic catalysts such as $SnCl_2$, $FeCl_3$, $Al_2(SO_4)_3 \cdot H_2SO_4$ and $BF_3 \cdot O(C_2H_5)_2$ has been studied.[296,297] According to,[297] $SnCl_2$ and $FeCl_3$ are not efficient (the polymer yield does not exceed 10 %). With the $Al_2(SO_4)_3 \cdot H_2SO_4$ complex poly(divinyl sulfide) is formed in yields up to 70 %. The optimum quantity of the catalyst is 1 %, the polymerization time being 7 hours. In solvents (heptane, benzene) the polymer yield drops sharply (8–10 %). The most efficient catalyst is BF_3 etherate (the polymer yield is up to 85 %). The polymers obtained are powders, insoluble in organic solvents, which swell in acetobutyrolactone and HMPA. The authors[297] consider poly(divinyl sulfide) as a heat-resistant polymer, since, by thermogravimetry, its mass loss in air at 200–220 °C is no more than 5 %. At 250–280 °C the polymers melt (evidently with decomposition, taking into consideration that the loss of mass begins already at 200 °C). The number of double bonds in the polymers is 30–55 % decreasing with an increase in the polymerization time. The authors[297] exclude, however, the formation of cyclic units and suggest the polymer to possess a cross-linked three-dimensional structure:

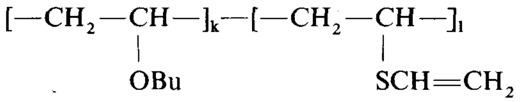


$$[-CH_2-\underset{\displaystyle SCH{=}CH_2}{\underset{|}{CH}}-]_n \left[\begin{array}{c} -CH_2-CH- \\ | \\ S \\ | \\ -CH-CH_2- \end{array}\right]_m$$

This structure is in agreement with the insolubility, but not with the fusibility of the polymers.

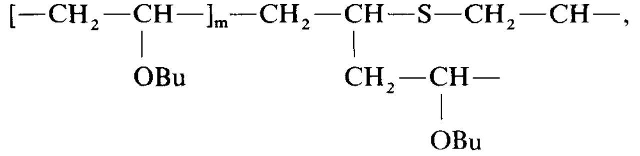
Copolymerization of DVS with chloroprene and butyl vinyl ether in the presence of $BF_3 \cdot O(C_2H_5)_2$ has been carried out.[297] In a 1:3 ratio of DVS:chloroprene a dark rubber-like mass, insoluble in organic solvents, is obtained. An increase of the amount of DVS in the starting mixture leads to insoluble powders. Also cross-linked rubber-like copolymers were obtained with butyl vinyl ether. These copolymers contain about 15 % DVS units (regardless of the composition of the monomer mixture).

The interest in the DVS/butyl vinyl ether copolymers is not without reason. The introduction of DVS units or blocks into the extended poly (butyl vinyl ether) chain, *i.e.*, the formation of copolymers with vinylthio side groups and branched structures of the type:



$$[-CH_2-\underset{\displaystyle OBu}{CH}-]_k-[-CH_2-\underset{\displaystyle SCH{=}CH_2}{CH}-]_l$$

and



$$[-CH_2-\underset{\displaystyle OBu}{CH}-]_m-CH_2-\underset{\displaystyle CH_2-\underset{\displaystyle OBu}{CH}-}{CH}-S-CH_2-CH-,$$

may impart the polymers with new valuable properties common to C—S bond containing compounds:[298] for instance resistance towards radiation, high adhesion, and anti-oxidative properties. The appearance of new biological properties in these copolymers is also rather possible since DVS and its lower oligomers are found in different types of garlic and display strong bactericidal activity.[28,29]

Thus, DVS oligomers of low molecular mass suggest themselves as bactericidal additives to process oils, for example, exposed to microorganisms and for the compounding of polymers on the basis of DVS with a wide spectrum of applications.

Taking all this into consideration, it was intended[299,300] to find a convenient synthetic route to soluble DVS/butyl vinyl ether copolymers. Some known methods for preparing butyl vinyl ether polymers and copolymers by cationic polymerization are not very suitable for the synthesis of copolymers with DVS since the latter forms with Lewis acids stable donor-acceptor complexes involving the sulfur atom, thus deactivating the catalyst.[301] Indeed, all attempts[299] to obtain DVS/butyl vinyl ether copolymers in the presence of $FeCl_3$ by conventional technique were unsuccessful. The catalyst introduced into the mixture of monomers underwent complexation and precipitated. No polymerization was observed. The copolymerization could only be performed when DVS was introduced into partially polymerized butyl vinyl ether, *i.e.*, at the propagation step.[299,300] This approach allowed soluble copolymers containing up to 8 mole % DVS to be prepared. The copolymerization was carried out under conditions close to those adopted for the commercial synthesis of poly(butyl vinyl ether): catalyst—butanolic $FeCl_3$ solution, temperature 20–70 °C. The order of mixing of the components is of primary importance. The catalyst is added to the butyl vinyl ether and only 20–40 minutes later DVS is added in portions with mixing, otherwise the copolymerization is completely inhibited by the formation of a stable catalyst-DVS complex.

The copolymers thus obtained are viscous resins readily soluble in various organic solvents. The formation of copolymers has been confirmed by the pattern of their solubility and turbidimetric titration curves corresponding to a monocomponent system.[300] This is indirectly proved by a decrease in the characteristic viscosity of the copolymers with increasing DVS content in the reaction mixture.

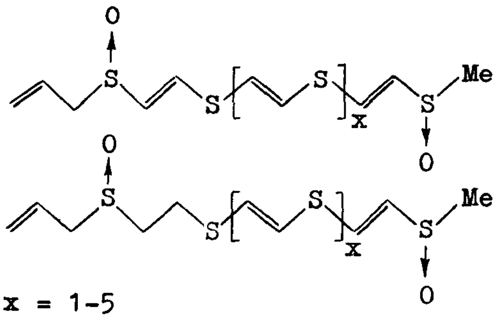
Contrary to[297] it is also possible to obtain liquid, soluble copolymers in the presence of $BF_3 \cdot O(C_2H_5)_2$.

With a 4-fold molar excess of DVS cross-linked copolymers are formed. This, however, regularly reduces both the reaction rate and degree of monomer conversion, since DVS is considerably less active in the cationic copolymerization than butyl vinyl ether. The process claimed can be envisaged as follows:[300] catalyst formation ($FeCl_3 + C_4H_9OH \rightleftharpoons H^+/FeCl_3C_4H_9O^-$), interaction of the catalyst and the monomer to form the carbocation (initiation) and the chain propagation. As has been established[300] the chain propagation of poly(butyl vinyl ether) under normal conditions takes 6–8 hours (the viscosity increases from 0.17 to 0.25 dl/g) and consequently 30–40 minutes after the start of the reaction there are enough macrocations in the system to involve DVS in the copolymerization. The chain break usually occurs by transfer to monomers, butanol, or by counterion protonation.

A method for the quantitative determination of vinylthio groups in copolymers by UV and IR spectroscopy has been developed.[302] The presence of free vinylthio groups in the copolymer has been found[300] to allow further polymerization of copolymers by radical initiation (azobisisobutyronitrile). The chain elongation is evident from the increase of the characteristic viscosity of the copolymer. Thus, the copolymer containing 7 % DVS upon heating with azobisisobutyronitrile for 10 hours changes its characteristic viscosity from 0.1 to 0.24 dl/g.[300]

VII.13 Biological Effects of Divinyl Sulfide

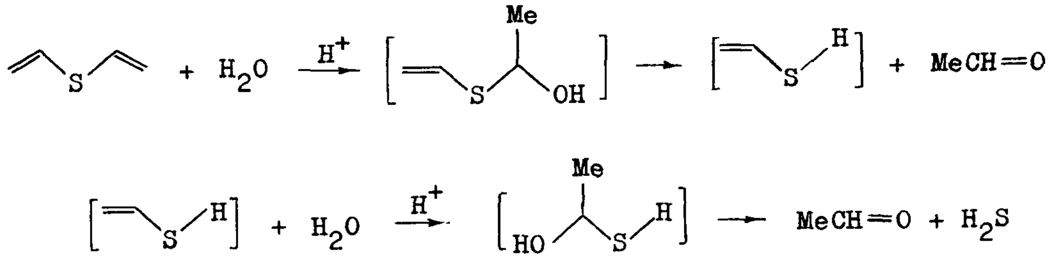
It is interesting that DVS was first mentioned[28] in connection with its isolation from a plant, the wild onion (*Allium ursinum L.*) or ramson. Later on, Zwergal[29] found DVS and a number of its derivatives in garlic (*Allium sativum*) and studied them in more detail. In his opinion, the active principle of garlic consists of DVS, vinyl allyl sulfoxide, $CH_2{=}CHCH_2S(O)CH{=}CH_2$, and their lower linear oligomers containing, according to the analytical data, poly(vinylene sulfide) blocks and allyl- and methylsulfinyl units as the terminal groups:



x = 1-5

Oligo(vinylene sulfides) of this structure possess a strong bactericidal effect.[29]

An organoleptic study of DVS has revealed its stability in an aqueous medium,[303] although according to our own observations DVS, when exposed to water and air, gelatinates within a few days. It is likely that in this case a neutral aqueous medium is meant, since at pH <7 DVS starts to hydrolyze to form acetaldehyde (or paraldehyde) and hydrogen sulfide.[304]



The hydrolysis rate is directly proportional to the acid concentration and changes with temperature in accordance with the Arrhenius equation.

The authors[303] note a direct relationship between the DVS concentration in water and the odor intensity. The DVS threshold concentrations in distilled and tap water are similar. The taste threshold for DVS is 1.8–2.1 mg/l. Consequently, the odor is the limiting feature of the hazardous effect of DVS according to the organoleptic factor.[303]

The effect of DVS on water quality management has been studied[303] by means of dynamic observations of biochemical oxygen consumption (BOC), nitrification, and saprophyte microflora development.[303] Within the concentrations studied (0.1–5.0 mg/l) DVS does not change pH, color, and transparency of water, and does not inhibit the development of saprophyte bacteria and simple organisms nor nitrification (observation time: 20 days). At 0.1–0.2 mg/l DVS does not appreciably affect the BOC_{20} dynamics, whereas the 0.5 mg/l level inhibits the BOC_{20} value by 15–16 % and at higher DVS levels (1–2 mg/l) BOC_{20} is inhibited by as high as 25–70 %.[303] This effect of DVS on BOC must be caused by concomitant oxidation of both DVS (formation of sulfoxide, sulfone, sulfinic acids) and DVS hydrolysis products (acetaldehyde, ethenethiol, hydrogen sulfide), although this is evidently not in full agreement with the above-mentioned[303] DVS stability in aqueous phase. The threshold DVS concentrations affecting the quality of stored water (according to the BOC_{20} index) are presented in.[303]

Upon intraperitoneal administration of DVS to mice and rats the LD_{50} are 112 (98.7–127) and 170 (145–198.5 mg/kg), respectively.[303] One of the characteristic symptoms of DVS intoxication is the depression of the central nervous system. Upon oral administration guinea pigs are more sensitive to DVS than mice and rabbits; rats being least sensitive. Administered to rats at a dose of 17 mg/kg for 1.5 months, DVS does not produce intoxication, lesions of the central nervous system, changes in the total blood count, peroxidase activity, serum catalase, and total blood cholinesterase. At the same time, the above dosage of DVS considerably increases the level of blood serum and liver hemogenate sulfhydryl groups. Simultaneously, some variation in the excretion of glucuronic acid in the urine, elevated levels of nitrogen, free amino acids and deceleration of the iodine-azide reaction rate occur. Moderate structural lesions in hepatic, myocardial, and renal tissue have been observed upon histopathological examination.[303] A study of cumulative properties has shown DVS to possess low cumulative potential.[303]

The embryotoxic effect of DVS administered subcutaneously to rats at a 35 mg/kg dose for one month before and during pregnancy has been investigated.[303] It has been established that prolonged administration of DVS does not kill the embryo and produces no changes in embryonal number, weight, and growth as well as placental mass and no macroscopic abnormalities. Consequently, DVS does not display any embryotoxic effect.

Prolonged intraperitoneal administration of DVS to rats at doses of 0.05, 0.5 and 10 mg/kg does not cause poisoning or any changes in weight gain. Two months after the start of the trial the rats given the 0.5 and 10 mg/kg doses show some change in their behavior reflex; however, this deviation levels off.[303] At all doses examined, DVS does not affect blood hemoglobin, leukocyte, erythrocyte, and differential blood count, as well as the total protein and urea levels of the blood serum.

In chronic trials two and six months after the start of the experiment the 0.5 and 10 mg/kg doses increase the content of both total and free sulfhydryl groups in the blood. In rats a change in the urine nitrogen and free amino acid level, the excretion of hippuric acid and an increase in the iodine-azide test time are observed.

The authors believe[303] the 0.05 mg/kg dose of DVS to be ineffective in the 6 month sanitary-toxic trial since this dosage produces no change in the indexes studied (integral, functional, biochemical, histological). According to the toxicometric parameters, DVS is close to cyclic sulfides.[303] The authors[303] suggest the 0.5 mg/l concentration of DVS as the highest acceptable for reservoir water, the organoleptic factor being the limiting hazardous sign.

For the determination of the highest acceptable DVS concentration in operation zone air a special trial was conducted.[305] The threshold DVS concentrations upon single inhalation, defined by the functional state of the central nervous system are as follows: in mice 25 mg/m^3 (according to the change in the spontaneous motor activity), in rats 12 mg/m^3 (according to the orientation reaction). In rats, upon chronic inhalation of DVS in a concentration of 9.8 ± 0.14 mg/m^3 for 4 months a depression of the central nervous system manifesting itself by loss of the defense reflex and depression of the orientation reaction is observed.[305]

Besides, changes in the blood serum alanineaminotransferase activity occur: one month after the start of the trial the activity decreases to 0.60 ± 0.24 μmole (1.26 ± 0.21 μmole in the control), 2.5 months later the picture normalizes and after 4 months the enzyme activity increases to 2.43 ± 0.17 μmole.[305] In the course of the trial an increase in the level of both total (42.45 ± 2.50) and free (29.32 ± 1.2) blood sulfhydryl groups as compared to the control (34.55 ± 1.9 and 21.70 ± 2.0, respectively) was observed; however, one month after the end of the trial these indexes normalize.[305] In rats and guinea pigs prolonged inhalation of DVS at 1.2 ± 0.5 and 1.1 ± 0.04 mg/m^3, respectively, produces no changes in the integral, functional, and biochemical indexes studied. Upon application of 50 % DVS solution in oil onto the skin of rats for one month neither dermatitis nor poisoning were observed.[305]

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