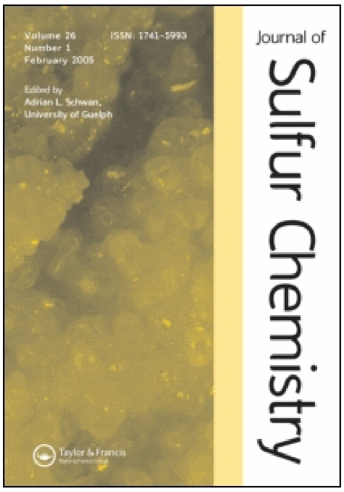

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CHALCOGENATION IN MULTIPHASE SUPERBASE SYSTEMS

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Superbase-promoted chalcogenation of diverse electrophilic reagents with the chalcogens or their anions in multiphase superbase systems became possible owing to the fact that under the action of a very strong hard base such as the "naked" hydroxide ion the elemental chalcogens produce softer and more nucleophilic species which successfully compete for the electrophiles. This explains the paradox that electrophiles such as acetylene, vinylacetylene, phenylacetylene, diacetylene and organo halides, in the presence of strong bases prefer to react with the chalcogens or their anions rather than with the activated hydroxide ion. Ignorance of this fundamental fact for a long time hindered progress in the application of chalcogens for the direct synthesis of their organic derivatives.

Key words: Chalcogenation, superbasic reductive systems, elemental sulfur, selenium and tellurium metal, acetylenes, organo halides.

CONTENTS

I. INTRODUCTION

Every chemist dreams to find the shortest way from the most available starting material to the target compounds. This review relates to this general problem.

We will try to reconsider from a uniform viewpoint new chalcogenation procedures developed in our laboratory during the last decade.[1-9]

Although the IUPAC nomenclature includes oxygen among the chalcogens (and we accept this idea), here, in this report, speaking of chalcogenation, we will discuss only sulfur, selenium, and tellurium reactions, since oxidation is a particular and very broad topic, which, of course, deserves special consideration.

Commonly (perhaps, not too precisely), chalcogenation is understood as any synthetic procedure introducing a chalcogen (in any oxidative state) into an organic molecule starting from any compound containing the element in question.

In our work we routinely utilize as anion suppliers elemental sulfur, hydrogen sulfide and inorganic sulfides, inorganic and organic polysulfides, selenium and tellurium metals, i.e. readily available, safe, and cheap starting materials.

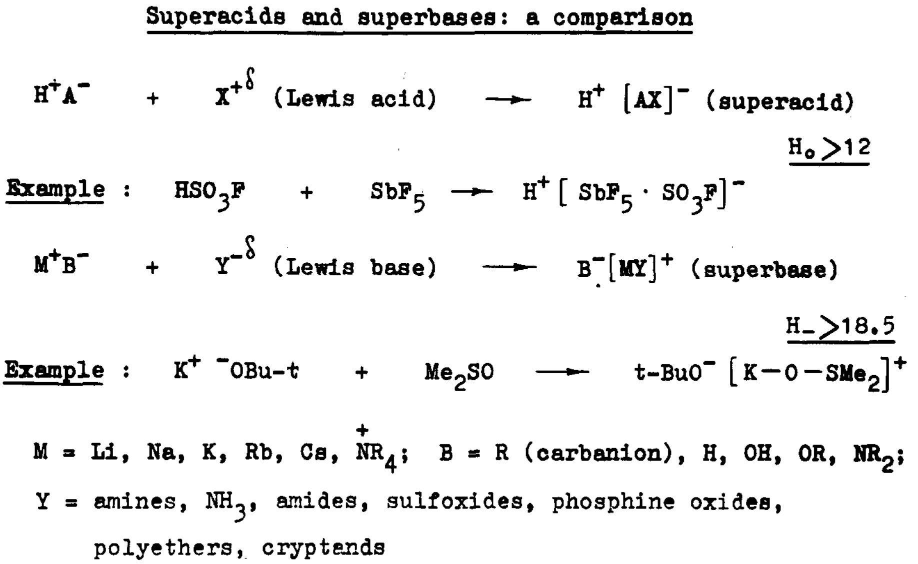
To capture the chalcogenide anions generated we use as electrophiles mainly acetylene and other alkynes as well as their synthetic equivalents such as vinyl halides and dihaloethanes and, to a lesser extent, alkyl halides. Acetylene and other alkynes such as vinylacetylene, phenylacetylene, and diacetylene as well as vinyl halides and dihaloethanes, are the cheapest and most accessible electrophiles because they are industrial large-scale products or by-products, the latter badly needing utilization.

To make the anionic chalcogenation most effective one has to generate the corresponding anions as desolvated and separated from their cations as possible; in most cases they must first be generated by cleavage of an element–element bond. For all this superbase media, catalysts, and reagents are required.

II. GENERATION OF SUPERBASE

The term "superbase media" has been systematically used by us since the middle of the 70's.[8] In the same period this term appeared in a monograph,[10] and in 1976, Normant and his group gave the name "hyperbasic media" to solutions of lithium dialkylamides in hexamethylphosphoric triamide (HMPA).[11]

Now the term superbase is currently used both in physical organic chemistry (*cf.*, *e.g.*,[12-14] and references therein) and in organic and organometallic synthesis (*cf.*, *e.g.*,[15,16] and references therein).



Superacids and superbases: a comparison

$H^+A^- + X^{+\delta}$ (Lewis acid) $\longrightarrow H^+[AX]^-$ (superacid)

$H_0 > 12$

Example : $HSO_3F + SbF_5 \longrightarrow H^+[SbF_5 \cdot SO_3F]^-$

$M^+B^- + Y^{-\delta}$ (Lewis base) $\longrightarrow B^-[MY]^+$ (superbase)

$H_- > 18.5$

Example : $K^+\ {}^-OBu\text{-}t + Me_2SO \longrightarrow t\text{-}BuO^-[K-O-SMe_2]^+$

M = Li, Na, K, Rb, Cs, $\overset{+}{N}R_4$; B = R (carbanion), H, OH, OR, NR_2;

Y = amines, NH_3, amides, sulfoxides, phosphine oxides, polyethers, cryptands

Scheme 1

According to[17] a superacid (Scheme 1) is defined as a complex acid formed from strong Lewis and Brønsted acids in a medium poorly solvating the proton. An example: "magic acid" from fluorosulfonic acid and antimony pentafluoride in sulfur trioxide.

By analogy, we have defined[6,7] a superbase as a complex base formed from a strong ionic base and a Lewis base capable to bind the alkali metal cation in a medium poorly solvating anions. An example: the superbase from potassium *t*-butoxide and dimethyl sulfoxide.

In other words, the essence of the superbasicity phenomenon consists of synergism of two or more bases resulting in an enhancement of the anion activity due to transformation of the cation into a bulky complex cation with delocalized charge. In the same vein the essence of the superacidity phenomenon consists of synergism of two or more acids resulting in enhancement of the proton activity due to the uptake of the conjugate anion into a bulky complex one.

Anions of superbases may be carbanions, hydroxide, hydride ion, alkoxides, and amides. Ligands for alkali metal cations which separate the ion pairs are usually other typical bases, including electron-donor dipolar nonhydroxylic solvents (sulfoxides, sulfones, amides, phosphine oxides), amines, ammonia, and polyethers, particularly macrocyclic ones.

Quantitatively, superacids are arbitrarily defined as media which are more acidic than 100% sulfuric acid ($H_0 > 12$). Since a similar convention for superbases was lacking, we defined them as media which are more basic (that is capable of ionizing weak acids to a higher degree) than saturated solutions of alkali metal hydroxides or alkoxides in water and alcohols, respectively ($H_- > 18.5$).[18]

Some typical representatives of superbase systems most often used for organic syntheses[11,14,18-31] are shown in the Table. It is seen that the pK_a values of conjugate acids for superbase media range from 30 to 40 logarithmic units which spans approximately the same interval of the acidity function (H_-) values.

Among the known superbases, two-phase systems such as an alkali metal hydroxide-dipolar nonhydroxylic solvent are believed to be most universal, available, stable, and convenient to handle. And among these the KOH/DMSO suspension is the champion.[6-8,18] This is a two-phase equilibrium system with a small content of the superbase

Table 1. Typical Superbases Used in Organic Synthesis

Superbase System	pK_a (H_-)	References
$NaNH_2/NH_3$ (liq)	32–40	19, 20
$LiNEt_2$/HMPA	38–40	11, 21
$LiN(Pr\text{-}i)_2/HN(Pr\text{-}i)_2$	40	14
$KHN(CH_2)_3NH_2/H_2N(CH_2)_3NH_2$ (KAPA)	40	22–24
KOH/DMSO	30–32	1–7, 18
NaOH/PTC[a]	34–41	25, 26
KOBu-*t*/DMSO	32	27
$NaCH_2SOMe$/DMSO	30	27
KCH_2SOMe/DMSO	35	27, 28
BuLi/KOAlk-*t*	40–43	29, 30
$NaNH_2$/NaOBu-*t*/THF	32	31

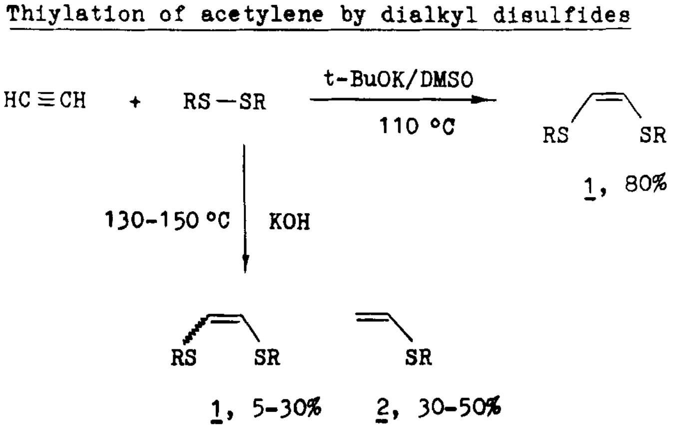
[a] PTC: Phase Transfer Catalysis

in the liquid phase which, when consumed, is to be continuously supplied from the solid phase, in this respect resembling phase-transfer catalytic processes. It is very important that the water molecules kept by excess KOH in the solid phase may gradually deliver protons (strictly after "demand") to convert the anions formed during the reaction into new stable molecules without any lowering of the basicity of the medium.[18]

Certain phase-transfer systems involving strong bases can also develop an acidity function H_- as high as 30 logarithmic units and higher in the organic phase and hence should be included in the superbase family.[18]

III. THIYLATION

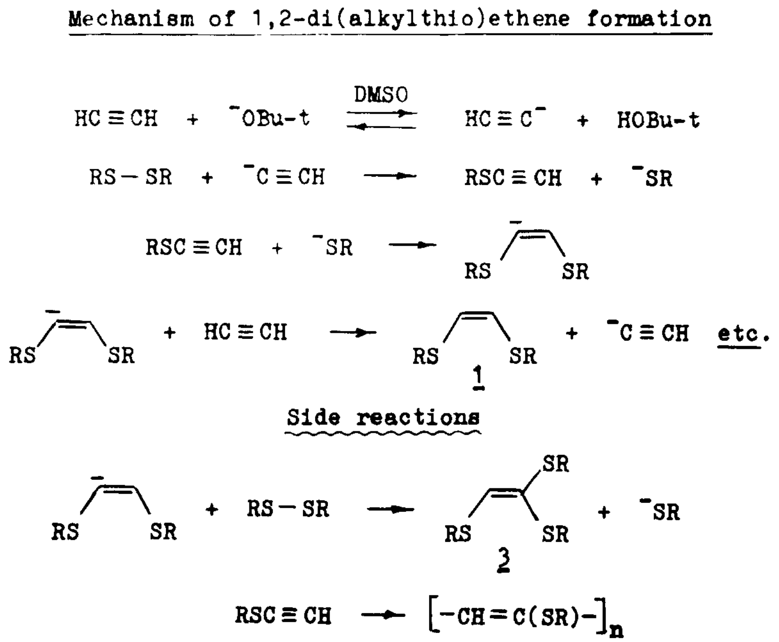
Our first experience of thiylation in the presence of superbase goes back to the early 70's when we encountered the superbase-catalyzed addition of organic disulfides to acetylenes affording 1,2-bis(alkylthio)ethenes **1** and/or vinyl sulfides **2** in good yields[1,32,33] (Scheme 2).



Scheme 2

With the *t*-BuOK/DMSO system as a catalyst the reaction proceeds smoothly at 110 °C to give selectively and stereospecifically *cis*-1,2-bis(alkylthio)ethenes **1** in yields of up to 80%,[33] whereas without the superbase system, the reaction is neither chemoselective nor stereospecific and normally requires a higher temperature to give lower yields of both products.[1]

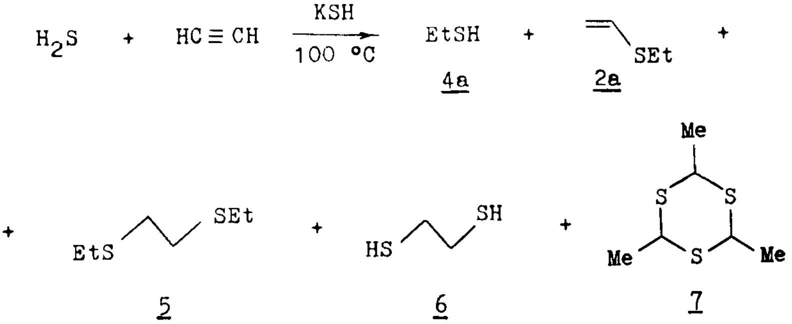
From the experimental data available the most probable mechanism of this reaction was proposed to be an anionic chain substitution-addition (Scheme 3): the acetylenic carbanion attacks the disulfide molecule to form the intermediate (alkylthio)acetylene and the corresponding alkanethiolate. These two species interact in accordance with the classic trans-nucleophilic addition scheme to give the intermediate *cis*-1,2-(alkylthio)ethenide anion which abstracts a proton either from acetylene or from *t*-butanol to afford the final product. The stereochemistry of this synthesis and the side products such as 1,2,3-tris(alkylthio)ethenes **3** and poly(alkylthio)acetylene are in keeping with this mechanism.[34]



Scheme 3

Almost all thiylation reactions in superbase media proceed via sulfide or hydrosulfide ions. It is quite clear that the most convenient source of these ions are hydrogen sulfide or its salts, the alkali metal sulfides. Thus, we have spent much effort on thiylations with these reagents. In spite of the fact that their reactions with electrophiles such as alkyl halides or oxiranes are traditional routes to sulfides or thiols, the thiylation of acetylenes in this way remained an ambiguous question for years.

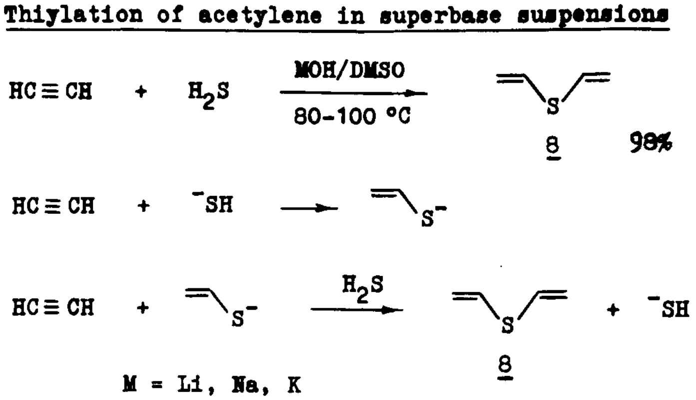
The known attempts by Reppe to add hydrogen sulfide to acetylene in the presence of potassium hydrosulfide led to a complex mixture of diverse organic sulfur compounds including ethanethiol **4a**, ethyl vinyl sulfide **2a**, 1,2-bis(ethylthio)ethane **5**, 1,2-ethanedithiol **6** and trimeric thioacetaldehyde **7** (Scheme 4). No divinyl sulfide was detected among the reaction products.[35]



Scheme 4

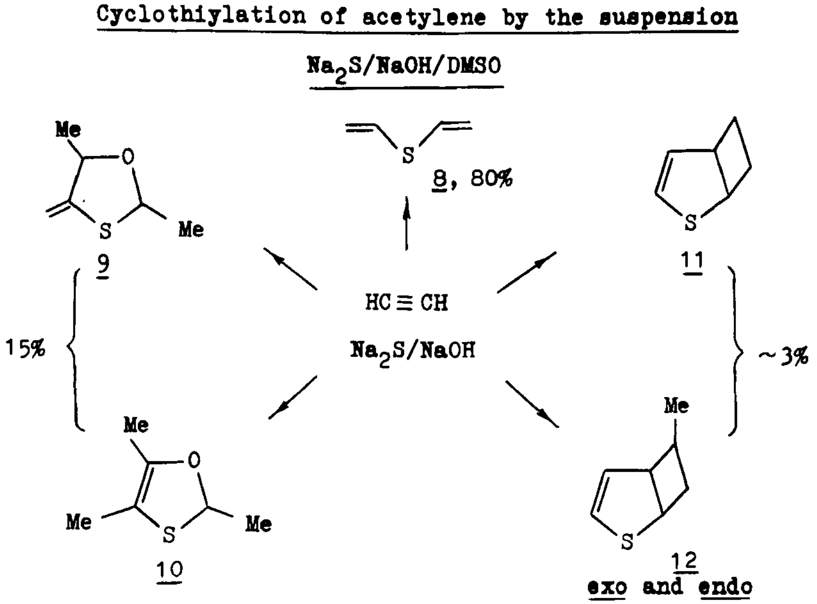
Only the superbase suspensions MOH/DMSO (*M* = Li, Na, K) allowed us in 1971[36] to carry out, cleanly and effectively, the expected addition of sulfide ions to acetylene to obtain divinyl sulfide **8** in almost quantitative yield (under optimal conditions).[4,5]

It is obvious that subsequent additions of the sulfide ion to two molecules of acetylene take place. The sulfide ions can be generated from both hydrogen sulfide or alkali metal sulfides or hydrosulfides (Scheme 5).[4,5]



Scheme 5

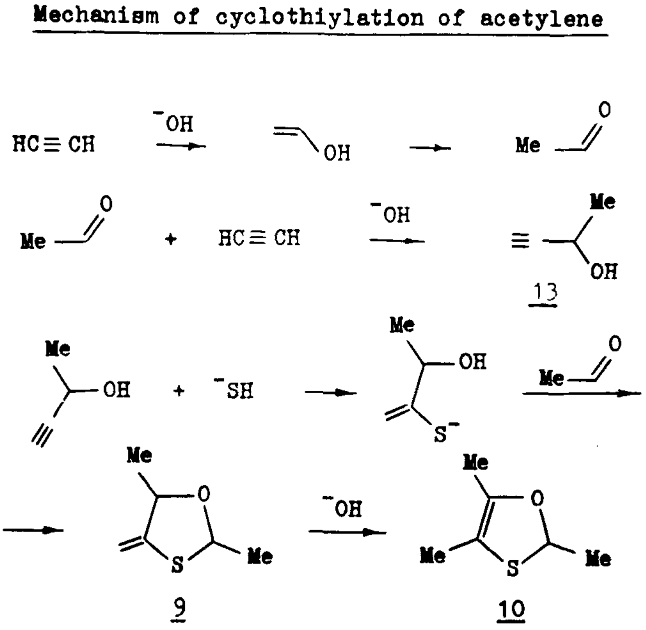
Sodium sulfide proves to be most useful for small-scale or laboratory preparation of sulfide **8** where no problems emerge with wastes whereas the H_2S-based process seems to be more attractive for industry since it is of a catalytic nature and, once initiated, requires nothing but hydrogen sulfide and acetylene.[4,5]



Scheme 6

Under certain conditions the addition of sulfide ions to acetylene is accompanied by unusual cyclooligomerization reactions (Scheme 6).[4,5] Thus, in the system Na_2S/NaOH/DMSO, together with the major product, divinyl sulfide, there are formed 2,5-dimethyl-4-methylene-1,3-oxathiolane **9** and its isomer 2,4,5-trimethyl-1,3-oxathiole **10** in a total yield of about 15%. Also, in the reaction there are commonly present three bridged sulfur heterocycles, 2-thiabicyclo[3.2.0]hept-3-ene **11** and its *exo*- and *endo*-6-methyl derivatives **12**. The methylation is brought about by DMSO.[4,5]

Just recently it became understandable how the first two heterocycles are formed (Scheme 7): acetylene is hydrated to acetaldehyde (through vinyl alcohol), the later is ethynylated to the acetylenic alcohol which then adds the hydrosulfide ion and one more molecule of acetaldehyde. The intermediate 3-methyl-1-butyn-3-ol **13** has been trapped in a similar process.[6,7,37]

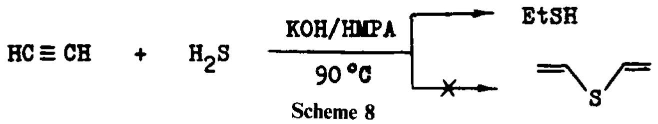


Scheme 7

Regardless of the modest yields of the heterocycles **9** and **10** their one-pot formation from very cheap raw materials makes them readily accessible for synthetic application.

It is interesting that the direction of a thiylation often profoundly depends on the nature of the complexing solvent (the ligand for the alkali metal cation). Thus, if DMSO is replaced by HMPA, then one can find conditions for the thiylation of acetylene with hydrogen sulfide under which ethanethiol **4a** is the only product instead of divinyl sulfide (Scheme 8).[38,39]

It follows that in HMPA the hydrosulfide ion is more desolvated than in DMSO, and, consequently, more amenable to single-electron transfer to the acetylene molecule to form the ion radical pair. The latter may dissociate to trigger the chain mechanism



Scheme 8

(Scheme 9). The anion radical of acetylene is reduced by hydrogen sulfide to afford vinyl anion and a thiol radical. The former then is quenched to ethylene which is further thiylated by the thiyl radical etc.[38]

$$HC\equiv CH + {}^{-}SH \longrightarrow [HC\equiv CH]^{\dot{-}}/\dot{S}H \rightleftharpoons [HC\equiv CH]^{\dot{-}} + \dot{S}H$$

$$[HC\equiv CH]^{\dot{-}} + H_2S \longrightarrow CH_2{=}CH^{-} + \dot{S}H$$

$$CH_2{=}CH^{-} + H_2S \longrightarrow CH_2{=}CH_2 + {}^{-}SH$$

$$CH_2{=}CH_2 + \dot{S}H \longrightarrow \dot{C}H_2{-}CH_2SH$$

$$\dot{C}H_2{-}CH_2SH + H_2S \longrightarrow EtSH + \dot{S}H$$

Scheme 9

The reactivity of the thiylating species generated from hydrogen sulfide in a superbase medium can be modified over a rather broad range not only by the choice of the ligand, but also by variation of the alkali metal cation which affects the ion-pairing and the solvation and hence the free energy of the anions.

In fact, when sodium or potassium hydroxide is replaced by lithium hydroxide in DMSO then yet another quite different thiylation of acetylene with hydrogen sulfide occurs. Neither divinyl sulfide, nor ethanethiol is formed in this case.[40] Instead, under very mild conditions (ambient temperature, atmospheric pressure), diethyl polysulfides **14** are formed, mainly the rather elusive tetra- and hexasulfide. It is highly amazing that no odd-membered polysulfides could be detected in the reaction mixtures (Scheme 10).[40]

$$HC\equiv CH + H_2S \xrightarrow[25\ ^{\circ}C]{LiOH/DMSO} \underset{\underline{14a\text{-}c}}{EtS_nEt}$$

$$n = 2\ (\underline{14a},\ 12\%),\ 4\ (\underline{14b},\ 34\%),\ 6\ (\underline{14c},\ 34\%)$$

Scheme 10

This mystery can be explained as follows. Because of the stronger solvation of the lithium cation, the hydrosulfide counterion is more naked and active as a reducing agent. Thus, the above sequence of anion-radical reactions leading to ethylene (Scheme 9) is highly facilitated. Due to the higher concentration of thiyl radicals at a lower temperature, their recombination, instead of thiylation, takes place to give disulfane. The latter, as a more reactive and stronger reducing agent, participates predominatingly in further transformations. Its oxidation by DMSO gives tetra- and hexasulfane, which, adding to ethylene, furnish diethyl di-, tetra-, and hexasulfide (Scheme 11).

Thus, the type of thiylation occurring in superbase media depends, often drastically, on the nature of the components. If in the system KOH/DMSO acetylene adds hydrogen sulfide to afford divinyl sulfide in high yield,[4,5] then on replacement of DMSO by HMPA the reduction to ethanethiol **4a** dominates[38,39] but when lithium is substituted for potassium (in DMSO) a quite different redox thiylation of acetylene takes place resulting in diethyl polysulfides in good yield.[40]

$$HC\equiv CH + {}^{-}SH \longrightarrow [HC\equiv CH]^{\dot{-}}/\dot{S}H$$

$$[HC\equiv CH]^{\dot{-}} + H_2S \longrightarrow CH_2{=}\bar{C}H + \dot{S}H$$

$$CH_2{=}CH^{-} + H_2S \longrightarrow CH_2{=}CH_2 + {}^{-}SH$$

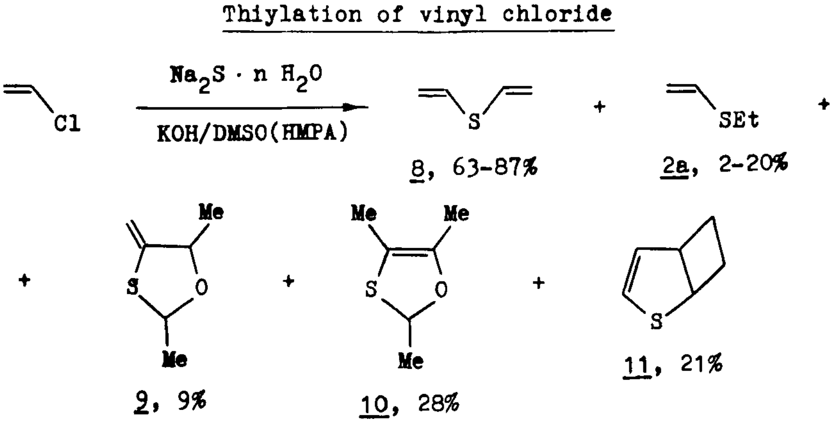
$$2\,\dot{S}H \longrightarrow H_2S_2$$

$$2\,H_2S_2 \xrightarrow{DMSO} H_2S_4 + H_2O$$

$$H_2S_4 + H_2S_2 \xrightarrow{DMSO} H_2S_6 + H_2O$$

Scheme 11

Vinyl chloride made from ethylene is now cheaper and more readily available than acetylene. Therefore, its thiylation, even with lesser yields of products, deserves attention. In the KOH/DMSO and KOH/HMPA systems the thiylation of vinyl halides with sodium sulfide gives mainly divinyl sulfide **8** in 63–87% yield. Ethyl vinyl sulfide **2a**, 2,5-dimethyl-4-methylene-1,3-oxathiolane **9**, 2,4,5-trimethyl-1,3-oxathiole **10** and 2-thiabicyclo[3.2.0]hept-3-ene **11** are also formed as side products (Scheme 12).[4,5]



Scheme 12

The most amazing feature of this reaction is that the yields of the sulfur heterocycles are much higher than in the case of acetylene: twice for the thiolanes **9** and **10** and by an order of magnitude for thiabicycloheptene **11**. The yield of the latter is already quite preparative. It rises with increasing KOH content in the reaction mixture and reaches 20% with a 2.5-fold molar excess of alkali relative to vinyl chloride. [41] This may well stimulate work on the chemistry of these highly interesting (both synthetically and theoretically) thiophene analogs.

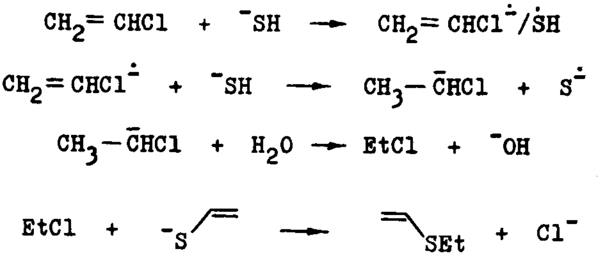
In HMPA the yield of divinyl sulfide decreases and that of ethyl vinyl sulfide increases which can be explained by a larger contribution of electron-transfer reactions. Even a small addition of HMPA to DMSO lowers the yield of divinyl sulfide by a factor of 1.5 and increases that of ethyl vinyl sulfide to over 10 times the value in pure DMSO.[4,5]

Typical inhibitors of radical processes such as hydroquinone, *N*,*N*-di-2-naphthyl-*p*-phenylenediamine, or phenyl-2-naphthylamine slow down the reaction:[41,42]

Inhibitor	Yield of divinyl sulfide, %
none	57
hydroquinone	39
N,*N*-di-2-naphthyl-*p*-phenylenediamine	19
phenyl-2-naphthylamine	26

This can be rationalized as an argument in favor of electron-transfer mechanisms.

One of the possible electron-transfer chains leading to ethyl vinyl sulfide is shown in Scheme 13.



Scheme 13

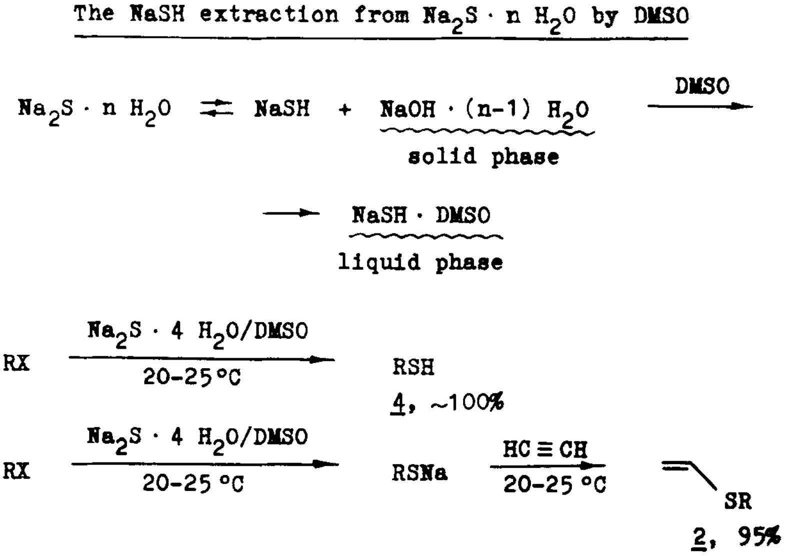
Acetylene is usually evolved as the reaction proceeds. Hence the expected elimination occurs. But under the same conditions, with acetylene the yield of divinyl sulfide is only 20%. This implies two competing thiylation paths: nucleophilic substitution of vinyl chloride (seemingly as a single-electron transfer process) and elimination–addition.[4,5,41,42]

Now it is time to take a closer look at the system $Na_2S \cdot n\ H_2O$/DMSO, one of the most effective thiylating reagents of the superbase type (Scheme 14).[6,7,18] As a matter of fact, upon mixing of sodium sulfide hydrates with DMSO, an unpredictable selective extraction of sodium hydrosulfide into the liquid phase takes place, obviously with formation of a complex with DMSO, sodium hydroxide remaining in the solid phase. One may separate the liquid phase to obtain a practically pure solution of sodium hydrosulfide in DMSO, the concentration of which can reach 1–1.5 mol/L. This is a very powerful thiylating reagent.[43]

The hydrosulfide ion activated in this way proves to be the actual thiylating agent in the synthesis of divinyl sulfides from acetylenes and sodium sulfide hydrates as follows from the kinetics study.[43,44]

In the reaction with organic halides the expected thiols **4** are formed in exellent yields (Scheme 14). They may be employed without isolation (as thiolates) in further synthetic steps. The best results are commonly achieved with sodium sulfide tetrahydrate, obtained by partial dehydration of the commercial nonahydrate.[43]

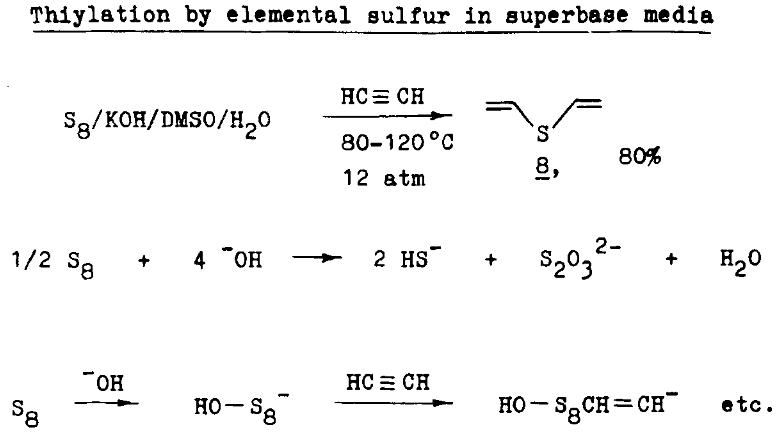
As an illustration, a one-pot synthesis of alkyl vinyl sulfides **2** directly from sodium sulfide, alkyl halides, and acetylene may be considered (Scheme 14). The reaction



Scheme 14

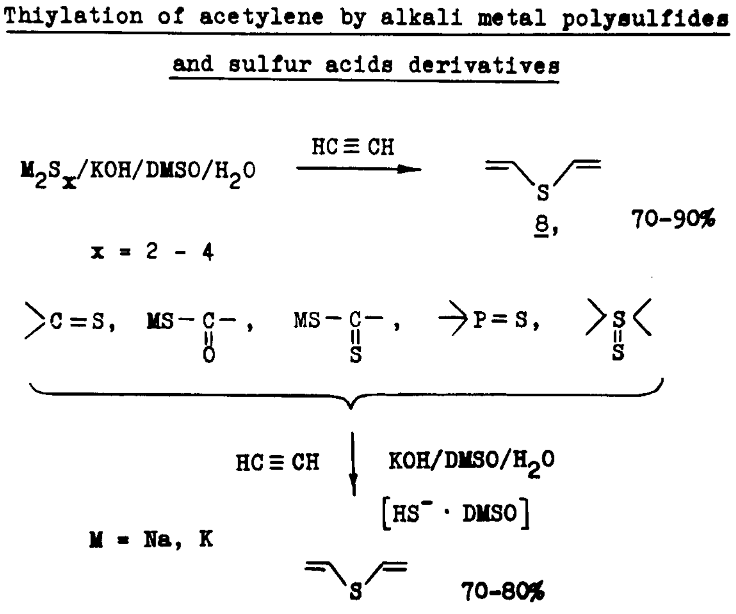
proceeds smoothly at ambient temperature and atmospheric pressure to give the target compounds in yields of up to 95%.[45] Today it is the simplest and most effective method for the preparation of thiols **4** and vinyl sulfides **2**, as well as of the starting sodium hydrosulfide.[43-45]

In the superbase suspensions KOH/DMSO or KOH/HMPA cyclooctasulfur is readily cleaved at 80–120 °C to form with acetylene the same products as in the case of sodium sulfide (Scheme 15).[46-48] Divinyl sulfide **8** can be prepared by this reaction in a yield of up to 80%, assuming that two sulfur equivalents give one equivalent of hydrosulfide ion. However, the true thiylating species may well be not the hydrosulfide anion, but rather polysulfides of higher nucleophilicity originating from the sulfur octamer.[46-48]



Scheme 15

Alkali metal polysulfides in the same superbase systems behave with acetylene like hydrosulfide ions to afford divinyl sulfide **8** in 70–90% (Scheme 16).[4]



Thiylation of acetylene by alkali metal polysulfides and sulfur acids derivatives

Scheme 16

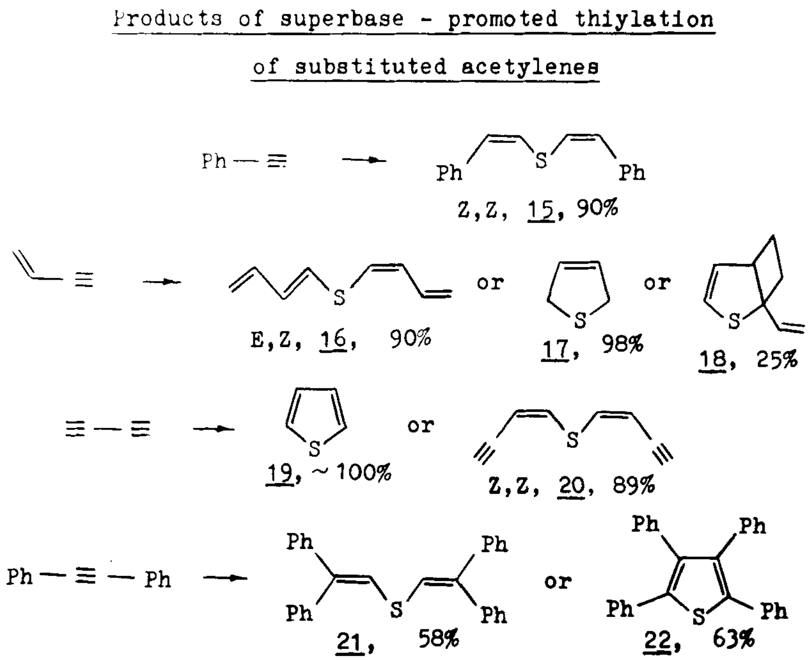
Diverse derivatives of thioacids including carbon disulfide, thiourea, esters, amides, or salts of thiocarbonic, thiocarboxylic, and thiophosphorus acids as well as sodium thiosulfate react with acetylene in a similar way affording divinyl sulfide in good yields (Scheme 16) (see[3] and references therein).

Apparently, all these compounds under the action of strong base undergo extensive cleavage to form the activated hydrosulfide ion which is the true thiylating agent in most of these cases.

In a two-phase superbase system consisting of triethylphosphine oxide and KOH the thioacetate anion AcS^- adds to phenylacetylene in the presence of small amounts of water to furnish di(*Z*-styryl) sulfide **15** as the final product in 90% yield.[49]

The first examples of phase-transfer catalysis in the addition of chalcogenide-centered anionic species to the triple bond were reported in,[50,51] where sulfide or ethanethiolate anions[50] or the thioacetate anion AcS^- [51] were shown to smoothly add to phenylacetylene in a strongly basic aqueous-organic medium in the presence of dibenzo-18-crown-6 or tetraalkylammonium salts to give the corresponding adducts.

All these versions of the superbase-promoted thiylation are more or less valid for substituted acetylenes or other electrophiles (Scheme 17). Now one can obtain:[3-5] di(*Z*-styryl) sulfide **15** from phenylacetylene; di(1,3-butadienyl) sulfide **16** of (*E*,*Z*) configuration, 2,5-dihydrothiophene **17**, or 1-vinyl-2-thiabicyclo[3.2.0]hept-3-ene **18** from vinylacetylene, depending on the reaction conditions; thiophene **19** or di(*Z*-1-buten-3-ynyl) sulfide **20** from diacetylene; bis(2,2-diphenylvinyl) sulfide **21** or tetraphenylthiophene **22** from diphenylacetylene. The yields are mostly good or excellent.



Scheme 17

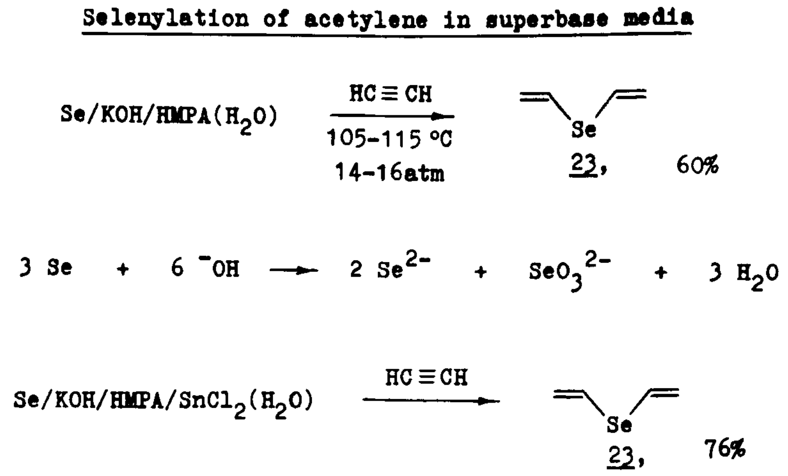
IV. SELENYLATION

In the systems KOH/DMSO or KOH/HMPA for the first time we have realized multiphase selenylation of acetylene by selenium metal (Scheme 18) to prepare divinyl selenide **23** in a yield of up to 60%, calculated on the assumption that three equivalents of selenium give two equivalents of selenide ions.[45,46] The following conditions were employed: the KOH/HMPA system, 105–115 °C, acetylenic pressure 14–16 atm. Apparently, under these conditions, selenium metal, like elemental sulfur, undergoes disproportionation to generate selenide or initially polyselenide ions or radical-ions which are captured by the acetylene.

When the special reducing agent ($SnCl_2$ or N_2H_4) is added to the reaction mixture, the yield of divinyl selenide **23** substantially increases up to 76% (Scheme 18).[52]

Under atmospheric pressure at 120–130 °C divinyl selenide can also be prepared in a yield of about 30%.[52,53] However, in contrast to sulfur, in highly concentrated aqueous alkali (12–14 mol per 1 mol of selenium), containing selenium metal and tin dichloride, but no complexing solvent at all, there are formed very active selenating species. This allows divinyl selenide to be prepared in a yield of up to 80% (Scheme 19).[54,55] In the absence of the reducing agent the yield of divinyl selenide drops to 33%.[55,56]

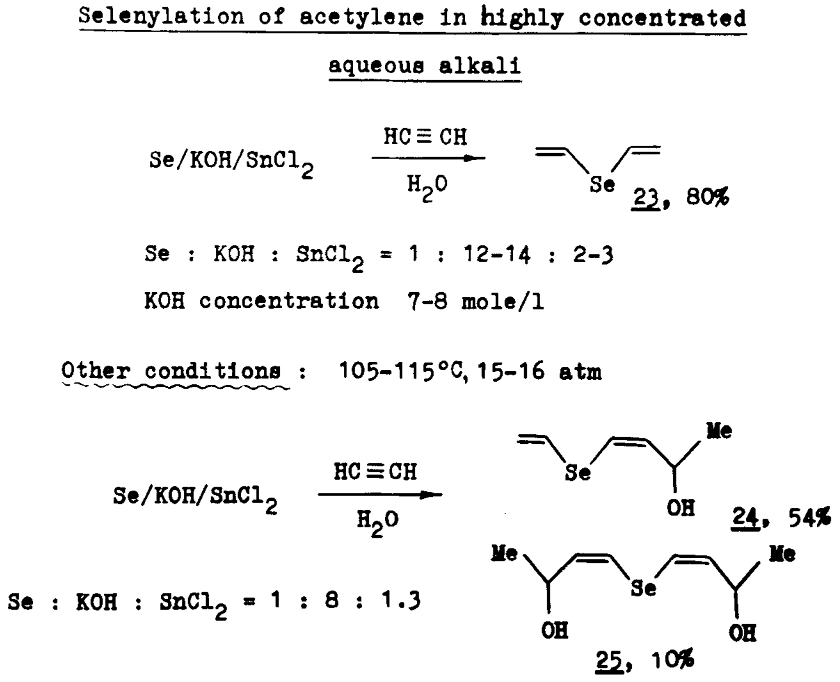
Under certain conditions, with a smaller alkali and tin dichloride content (eight equivalents of alkali instead of twelve per one equivalent of selenium and half the amount of $SnCl_2$), the selenylation predominatingly takes a different path (Scheme 19) affording hydroxyethylated divinyl selenide, (*Z*)-1-vinylseleno-1-buten-3-ol **24**, in a yield exceeding 50% and small amounts of the corresponding diol **25**.[57-60] Here, we again



Scheme 18

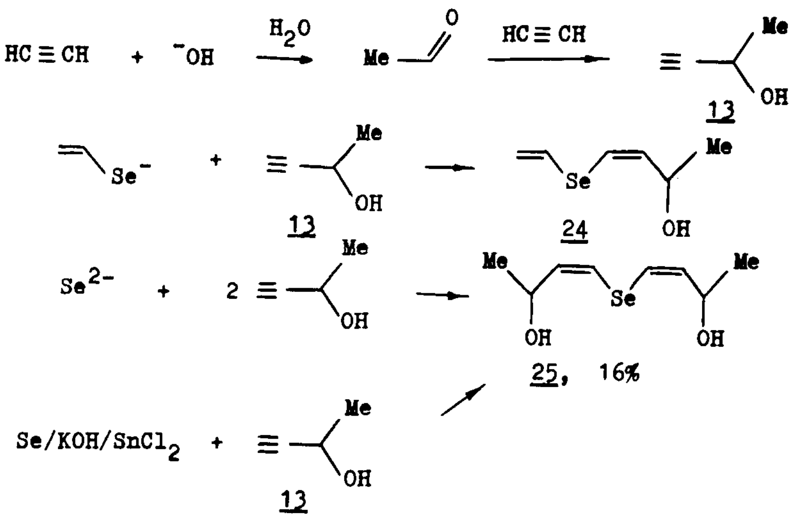
encounter the hydration of acetylene to 3-methyl-1-butyn-3-ol 13[6,37] (Scheme 20) which then is attacked by selenide or vinylselenide anions. This was proved, under the same conditions, by direct selenylation of this alkynol, leading to the expected selenadiol in 16% yield.[56–59]

Thus, the synthetically very promising functionalized divinyl selenides **24** and **25** are



Scheme 19

Selenylation of acetylenic alcohols

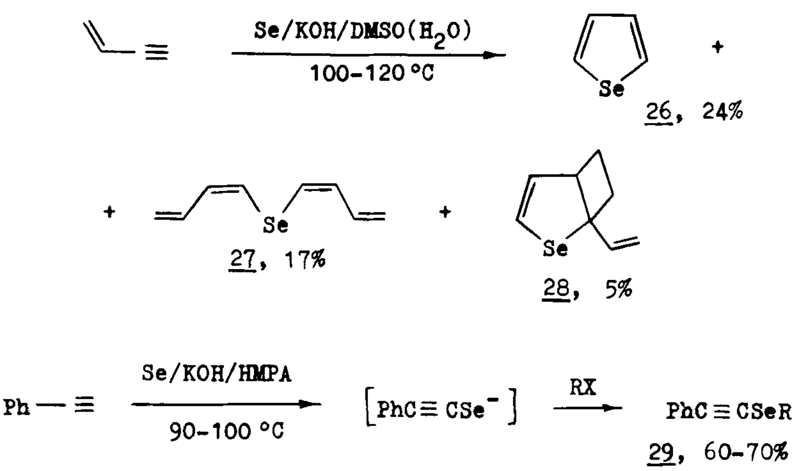


Scheme 20

now becoming readily accessible through the selenylation of both acetylene and acetylenic alcohols.

The selenylation of vinylacetylene by the superbase suspension of selenium metal and KOH in DMSO gives selenophene **26**, di(1,3-dibutadienyl) selenide **27**, and 1-vinyl-2-selenabicyclo[3.2.0]hept-3-ene **28** in yields of 24, 17, and 5%, respectively (Scheme 21).[47,48]

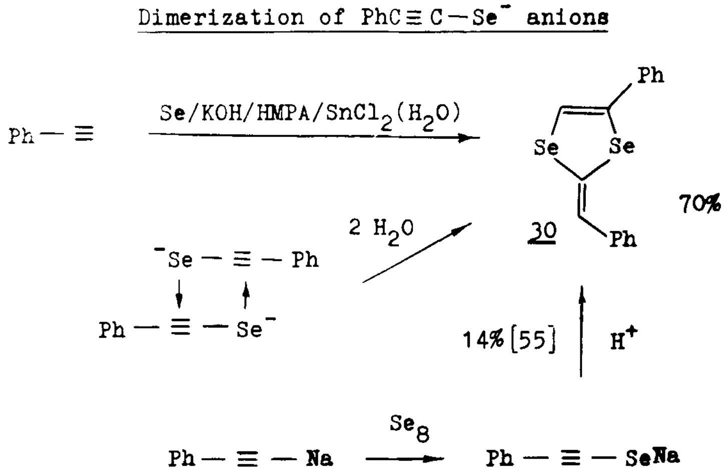
Selenylation of vinylacetylene and phenylacetylene



Scheme 21

Phenylacetylene with the suspension Se/KOH/HMPA (a three-phase system), under anhydrous conditions generates phenylethynylselenide anions, which can be trapped by an appropriate electrophile, say, an alkyl halide, to furnish alkyl phenylethynyl selenides **29** in good yields (Scheme 21). At present, this is the shortest way to acetylenic selenides.[61,62]

If the selenylation of phenylacetylene is carried out in the presence of water and $SnCl_2$ the anticipated distyryl selenides are not formed (Scheme 22). Instead, (*Z*)-2-benzylidene-4-phenyl-1,3-diselenole **30** is isolated in a yield of up to 70%.[61-63] This heterocycle likely results from dimerization of the already considered phenylethynylselenide ion. Just for this process two molecules of water are required as the proton source (Scheme 22). This heterocycle **30** was first obtained in 14% yield by Mayer *et al.* by acidification of sodium phenylethynylselenide prepared from the corresponding acetylide (Scheme 22).[64] As expected, similar results are obtained under typical phase-transfer conditions.[65]

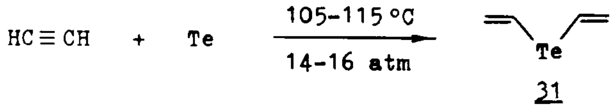


Scheme 22

V. TELLURYLATION

Tellurium metal in the suspension KOH/HMPA (H_2O) acts as a powerful tellurylating reagent.[47,48,58] When acetylene is used as an electrophile, divinyl telluride **31** is formed in a yield of 67% (Scheme 23). Like in the selenium case, $SnCl_2$ as the reducing agent makes the reaction more facile increasing the yield of divinyl telluride up to the theoretical value basing on the redox equation where 3 equivalents of tellurium give 2 mol of telluride ions. And also like in the selenium case, tellurium metal in multiphase systems with highly concentrated aqueous potassium hydroxide performs even better than with HMPA to afford divinyl telluride in a yield of 94%, calculated on the assumption that 1 equivalent of tellurium gives one mol of divinyl telluride, *i.e.* 1.5 times higher than in HMPA.[66,67] An explanation of this fact is that selenide and telluride ions or radical ions are stronger nucleophiles than sulfide ions due to their size and lesser solvation.

Tellurylation of acetylene by metallic tellurium under strongly basic conditions



31

Base	Yield, %
KOH/HMPA(H_2O)	67
KOH/HMPA/$SnCl_2$(H_2O)	100
KOH/H_2O/$SnCl_2$	94
1 : 6-7 : 2-3, moles	

Redox eq.

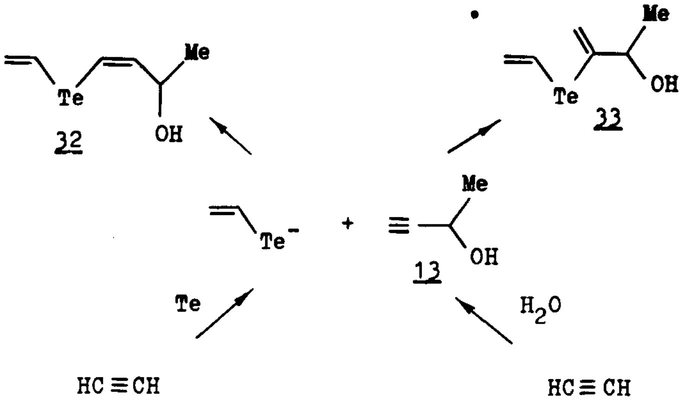
$$3\,Te \rightarrow 2\,Te^{2-} + Te^{4+}$$

$$2\,Te \xrightarrow{SnCl_2} 2\,Te^{2-}$$

Scheme 23

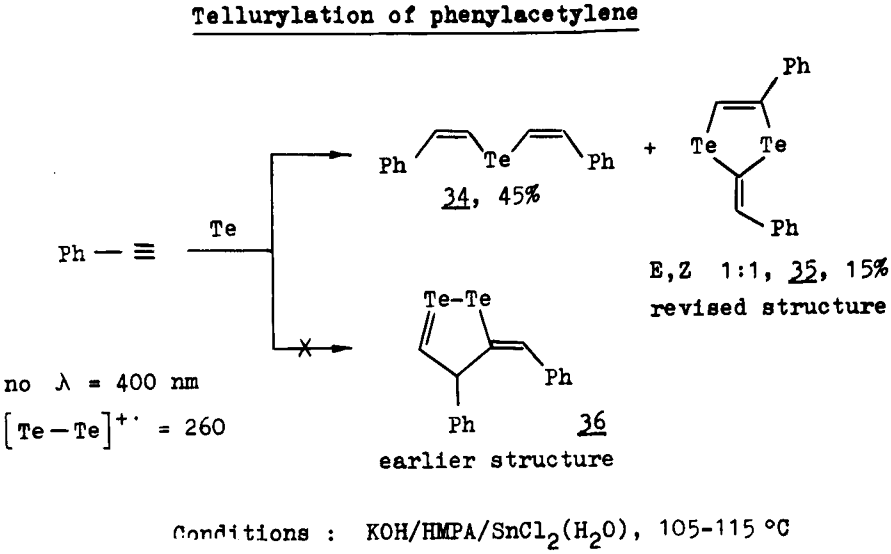
Similar to the reaction with selenium, the tellurylation of acetylene in the presence of water is also accompanied by the formation of the hydroxyethylated divinyl tellurides **32** and **33**, although in lower yield (5%) (Scheme 24).[57,67,68] This is a result of telluride ion addition to the 3-methyl-1-butyn-3-ol **13**, the product of the side-reaction hydration of acetylene.[6,37]

Side products of the acetylene tellurylation



Conditions: Te/KOH/$SnCl_2$/H_2O, 105-115 °C
1 : 6 : 1-2 : 40 mole

Scheme 24



Scheme 25

When phenylacetylene is heated with tellurium metal in the multiphase suspension KOH/HMPA/$SnCl_2$/H_2O at 105–115 °C, di(*Z*-styryl) telluride **34** and 2-benzylidene-4-phenyl-1,3-ditellurole **35** are formed in yields of 45 and 15%, respectively (Scheme 25).[61,69] As in the selenylation of phenylacetylene, the latter is generated by the dimerization of the intermediate phenylethynyltelluride anion. Likewise, the multiphase reaction of tellurium with phenylacetylene in a highly basic $N_2H_4 \cdot H_2O$/KOH/toluene system in the presence of a quaternary ammonium salt gives di(*Z*-styryl) telluride in 50% yield.[65]

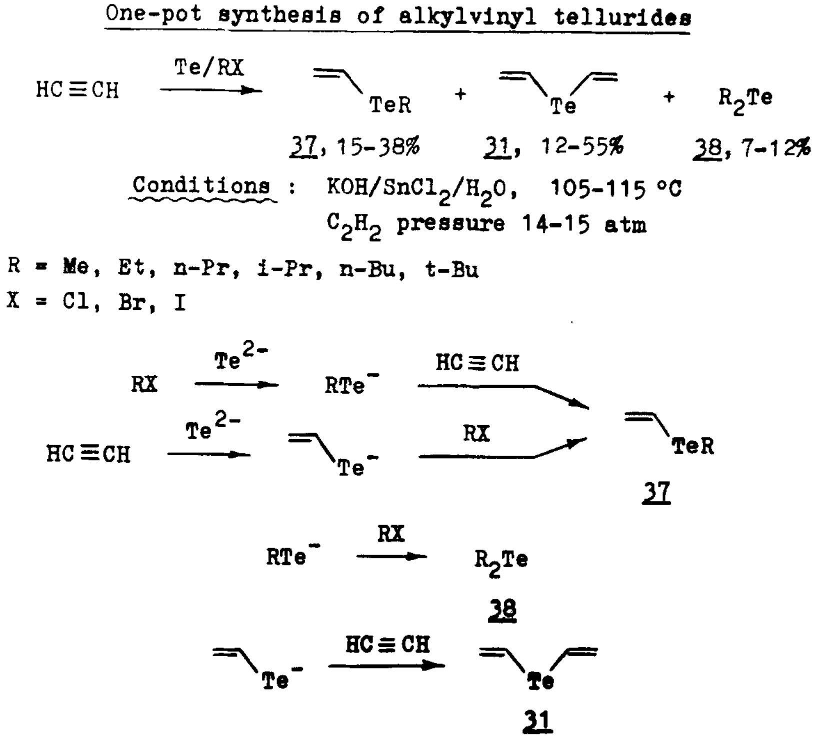
Earlier,[61] relying on IR, NMR, and mass spectra we believed that the heterocycle formed in this reaction was 3-benzylidene-4-phenyl-1,2-ditellurole **36**. The chief argument for this was the Te–Te ion in the mass spectrum, since all other spectral patterns fitted both structures. However, recently Singh and Wudl[69] provided evidence in favor of the normal 1,3-ditellurole structure **35** (*i.e.* just the same as in the selenium case).[61-63]

We also have developed a convenient and effective route to alkyl vinyl tellurides **37** by direct multiphase reaction of tellurium metal, acetylene, and an alkyl halide at 105–115 °C in the strongly basic reducing system KOH/$SnCl_2$/H_2O (Scheme 26).[70,73]

Apart from the desired alkyl vinyl tellurides **37**, there are also formed divinyl telluride **31** and the corresponding dialkyl tellurides **38**.

In this reaction two electrophiles, the alkyl halide and acetylene, compete for the telluride ions. In the first stage both reactions lead in the same direction, since both alkanetellurolate and vinyltelluride anions can be cross coupled to the alkyl vinyl telluride. The symmetric tellurides result from coupling of the intermediates with another mole of the same electrophile.

Under identical conditions the overall yield and ratio of the tellurides **31**, **37**, and **38** significantly depend on the starting alkyl halides. The best results are obtained with primary and secondary alkyl bromides allowing the preparation of alkyl vinyl tellurides in a yield of 33–38%.[71-73]



Scheme 26

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