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THERMAL METHODS FOR THE SYNTHESIS OF THIOPHENE, SELENOPHENE, AND THEIR DERIVATIVES. (REVIEW)

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The literature data concerned with thermal reactions producing thiophene, selenophene, and their derivatives are systematized and reviewed. The mechanisms of these reactions are examined and conditions for the formation of thiophene and selenophene heterocycles are formulated.

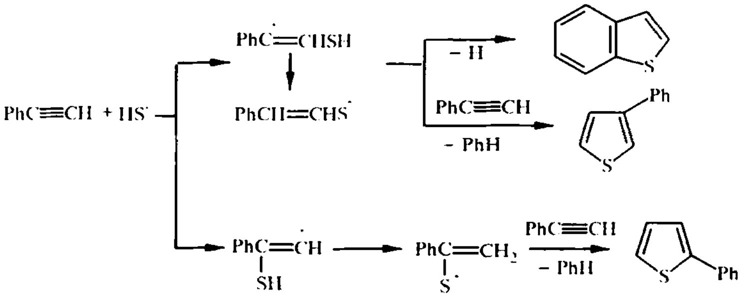
Keywords: thiophene, selenophene, thermal synthesis, mechanism.

Thiophene, selenophene, their derivatives and analogs are used for the preparation of thermally stable and electrically conducting polymers, medicinal and veterinary preparations, pesticides, complexing agents,etc.[1, 2]. A number of compounds of this type are difficult to obtain, because their synthesis frequently involves many stages and requires the use of catalysts [3-6]. In contrast, many thermal reactions of hydrogen sulfide, dihydrocarbyl disulfides, selenides and diselenides with unsaturated and aromatic compounds are simple one step methods for the synthesis of thiophenes, selenophenes, their derivatives and analogs. The literature data concerned with these reactions are examined and systematized and their mechanisms and prospects in organic synthesis are discussed below. Publications by the authors of this review, which reflect many years of research, occupy an important position in this review.

REACTIONS OF HYDROGEN SULFIDE AND ALKYLCHALCOGENIDES

Chalcogen-centered radicals are formed in the thermal reactions of hydrogen sulfide and many organic sulfur and selenium compounds. These radicals react more or less readily with unsaturated and aromatic compounds to give radical adducts which frequently heterocyclize to give thiophene or selenophene rings [7-9].

Scheme 1



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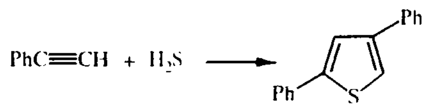
Hydrogen sulfide and acetylene do not react at 400-700°C. The gas phase reaction of phenylacetylene with hydrogen sulfide gave benzothiophene, 2- and 3-phenylthiophene in an overall yield of not more than 5-10% [10]. Their formation (scheme 1) is apparently explained by the addition of the HS· radicals predominantly at the β-position of the phenylacetylene triple bond, since the yield of 2-phenylthiophene is considerably less than that of 3-phenylthiophene. The yields of the phenylacetylene sulfuration products were increased when dialkyl disulfides were used instead of hydrogen sulfide.

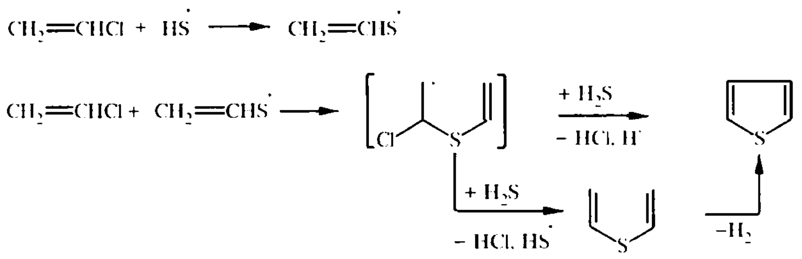
Phenylacetylene reacted in a different way with hydrogen sulfide in the presence of sulfur in the liquid phase at 150°C to give 2,4-diphenylthiophene (reaction 1, 80% yield) [11]:



(1)

Vinyl radicals were formed when hydrogen sulfide reacted with chloroethene in the gas phase (530-550°C) and these radicals reacted further to give thiophene (scheme 2) [12, 13]:

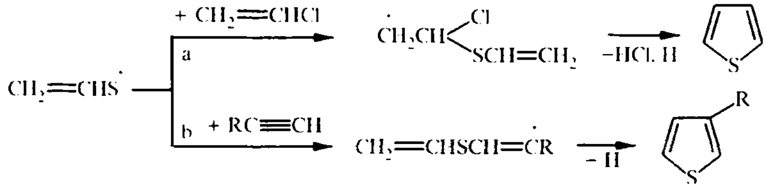
Scheme 2



The yield of thiophene could be increased to 80% by using a 2-3 fold excess of chloroethene.

Gas phase thermolysis (500-570°C) of chloroethene-hydrogen sulfide-acetylene (or substituted acetylenes) mixtures gave thiophene or substituted thiophenes as a result of concurrent reactions of vinylthiyl radicals with the two chemical traps $CH_2{=}CHCl$ and $CH{\equiv}CH$ [14]. In the second step the vinylthiyl radicals can react in two parallel directions (scheme 3): a) with chloroethene to give thiophene, and b) with acetylene to give thiophene also:

Scheme 3



R = H, Me, Ph

In the ternary hydrogen sulfide-chloroethene-acetylene system thiophene is formed by addition of the radicals to acetylene. The latter is a more effective chemical trap than chloroethene, since the yield of thiophene reached 73-80% with equivalent amounts of the reagents and even when $CH_2{=}CHCl$ was in deficit and its conversion did not exceed 78%.

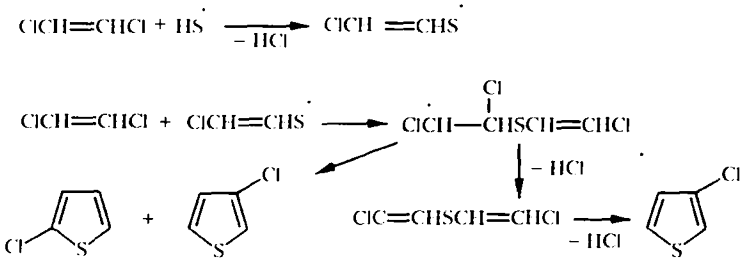
The main products in the reaction of chloroethene with hydrogen sulfide and methylacetylene were 2- and 3-methylthiophene (overall yield about 80%) and thiophene (13-16%). Like acetylene, methylacetylene is a more effective trap for the $CH_2{=}CHS$· radicals than chloroethene. These radicals attack the α- and β-atoms of the triple bond of methylacetylene equally (the yields of 2- and 3-methylthiophene are identical). Nevertheless, methylacetylene is a less effective trap for vinylthiyl radicals than acetylene.

The reaction of chloroethene with hydrogen sulfide and phenylacetylene gave 3-phenylthiophene (yield up to 63%). 2-Phenylthiophene (12-16%) and benzothiophene (4-16%) were also obtained. The absence of thiophene in the reaction products indicates that phenylacetylene was the sole trap for the $CH_2{=}CHS\cdot$ radicals. The effectiveness of the chemical traps for the vinylthiyl radicals increases in the order:

$$CH_2{=}CHCl < MeC{\equiv}CH < HC{\equiv}CH < PhC{\equiv}CH$$

The reaction of hydrogen sulfide with 1,2-dichloroethene at 430-470°C gave a mixture of 2- and 3-chlorothiophene with an overall yield of 30-35%. They are formed as a result of the β-chlorovinylthiyl radicals generation which then react with dichloroethene as follows (scheme 4) [15-16]:

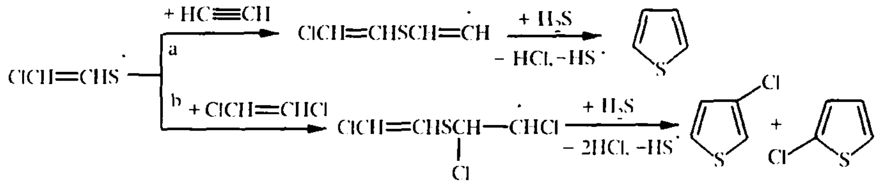
Scheme 4



The yield of chlorothiophenes is increased with an excess of dichloroethene.

The basic product of the 1,2-dichloroethene, hydrogen sulfide, and acetylene co-pyrolysis at 500-600°C (1:1:1 molar ratio) is thiophene (up to 40% yield), while 2- and 3-chlorothiophene are formed in only 10-15% yield [14]. This shows that β-chlorovinylthiyl radical adds predominantly to acetylene (scheme 5,a) rather than to dichloroethene (scheme 5,b).

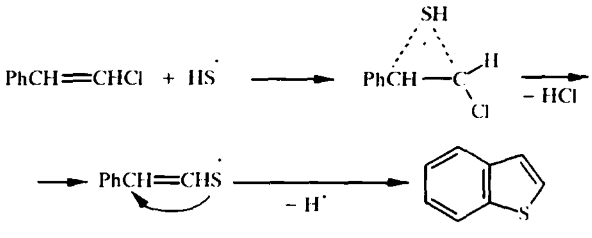
Scheme 5



Minor products from the reaction were thienothiophene (2-5%) and benzo[*b*]thiophene (~ 3%).

Hydrogen sulfide reacts with β-chloro- or β-bromostyrene in the gas phase at 600°C to give benzothiophene as a result of intramolecular cyclization of the β-phenylvinylthiyl radicals generated *in situ* (scheme 6) [17]:

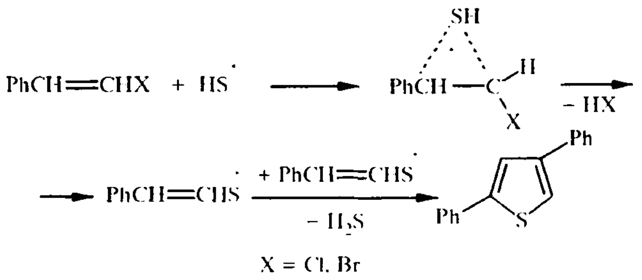
Scheme 6



The yield of benzothiophene reached 75-85%. Alkanethiols can be used in place of hydrogen sulfide.

The reaction of β-halogenostyrenes with hydrogen sulfide at 150-170°C (scheme 7) gave only 2,4-diphenylthiophene which is the product of intermolecular condensation of β-phenylvinylthiyl radicals [18]:

Scheme 7

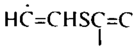


Pyrolysis of the β-halogenostyrene–hydrogen sulfide–acetylene (or phenylacetylene) ternary system gives benzothiophene as the major product, but also 2- and 3-phenylthiophene [14]. So the basic product of the β-chlorostyrene–hydrogen sulfide–acetylene system thermolysis at 580-650°C is benzo[*b*]thiophene (52% yield). 3-Phenylthiophene (4% yield) and 2-phenylthiophene (2-3%) are the products of the β-phenylvinylthiyl radical addition to acetylene. Thiophene (5-30% yield) is apparently formed by the addition of vinylthiyl radicals to acetylene. Thermolysis of the α-bromostyrene–hydrogen sulfide–acetylene system at 500-525°C gave predominantly 2-phenylthiophene (73% yield) which is the product of the β-phenylvinylthiyl radicals addition to acetylene. The main products of the thermolysis of the β-chlorostyrene-hydrogen sulfide-phenylacetylene system (1:1:1 molar ratio) at 650°C are benzothiophene (45% yield) and 3-phenylthiophene (12% yield, 3 times as large as when acetylene was used). Traces of 2-phenylthiophene (up to 2%) and a considerable amount of benzene (33%) are also formed. On the whole, the first step in the thermolysis of the β-halogenostyrene–hydrogen sulfide–acetylene (or phenylstyrene) ternary systems is the generation of β-phenylvinylthiyl radicals, intramolecular cyclization of which leads to benzo[*b*]thiophene. The reaction of PhCH=CHS· radicals with acetylene or its derivatives occurs more slowly than heterocyclization. Under these conditions the radicals effectively do not react with halogenoethenes. Phenylacetylene is a more effective trap than acetylene for these radicals. In contrast, α-phenylvinylthiyl radicals react predominantly with acetylene to give 2-phenylthiophene. A comparison of the radical-adducts of vinylthiyl radicals with phenylacetylene (**1**-**4**) shows that the phenyl groups in radicals **1** and **3** are most involved in delocalization of the unpaired electron.

$CH_2{=}CHSCH{=}\dot{C}Ph$ **1**

$PhCH{=}CHSCH{=}\dot{C}H$ **2**

$PhCH{=}CHSCH{=}\dot{C}Ph$ **3**

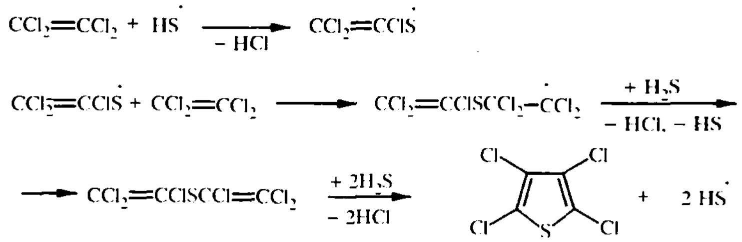


$H\dot{C}{=}CHSC(Ph){=}CH_2$ **4**

This is evidently why phenylacetylene is the most effective chemical trap for vinylthiyl radicals. β-Phenylvinylthiyl are less selectively trapped by acetylene and its derivative because of the possibility for intramolecular cyclization to the thermodynamically stable heterocycles and also the formation of a less stabilized radical-adduct. β-Phenylvinylthiyl radicals react with acetylene in the same way as unsubstituted vinylthiyl radicals. β-Chlorovinylthiyl radicals add selectively to acetylene with formation of 2- and 3-chlorothiophene.

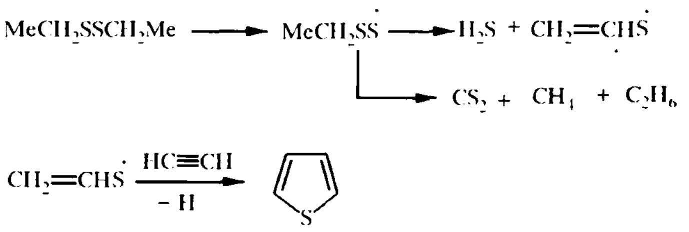
The reaction of tetrachloroethene with hydrogen sulfide at 400-600°C gave tetrachlorothiophene (scheme 8). A yield of 75% was achieved when starting materials and intermediate products were recycled. The conversion of tetrachloroethene in one pass is very low in consequence of the low reactivity of tetrachloroethene with respect to vinylthiyl radicals [19]:

Scheme 8



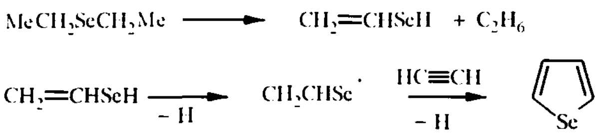
The basic product in the reaction of dimethyl disulfide with acetylene at 480-500°C is thiophene (45-50% yield). It is formed as a result of addition to acetylene of vinylthiyl radicals generated by the pyrolysis of Et_2S_2 (scheme 9) [20]:

Scheme 9



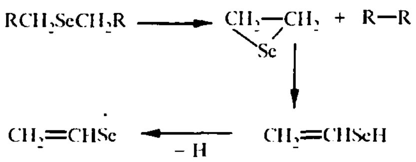
Vinylselenyl radicals add more selectively to acetylene. Thermolysis of dialkyl selenides is an effective source of these radicals. Selenophene was obtained in yields up to 98% (R = Et) from the gas phase reaction of RSeR (R = Et, Pr, Bu) with acetylene (400-600°C, molar ratio of reagents 1:1-3) (scheme 10) [21, 22]:

Scheme 10

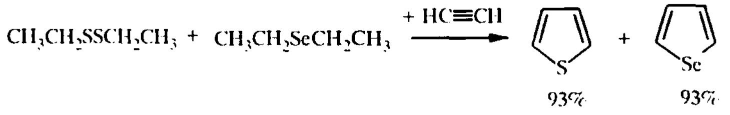


The yield of selenophene was less (70-77%) when larger dialkyl selenides (Pr_2Se, Bu_2Se) were used. Formation of selenophene is explained by thermal scission of alkyl groups with formation of vinylselenyl radicals (scheme 11):

Scheme 11



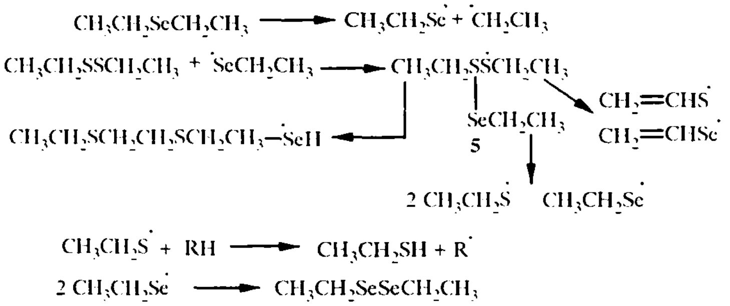
When acetylene was thermolyzed with a mixture of Et_2S_2 and Et_2Se (molar ratio 1 : 0.2-1, 470-510°C) thiophene and selenophene were formed simultaneously (reaction 2) with the yield of each reaching 93% [23, 24].



(2)

The synergism of the formation of these diethyl chalcogenides was confirmed from their thermolysis and co-thermolysis. For example at 580-600°C Et$_2$S$_2$ gave only 5% of thiophene together with a mixture of thienothiophene and carbon disulfide [25]. At 360-400°C Et$_2$Se was converted predominantly to Et$_2$Se$_2$ (up to 60% yield) and selenophene (5%). At 430°C Et$_2$Se is completely degraded to elemental selenium and gaseous products. In the absence of acetylene the co-thermolysis of Et$_2$S$_2$ and Et$_2$Se at 370-430°C gave organosulfur compounds predominantly. For example, at 370°C the basic reaction products were EtSH (73% yield), thiophene (4%), and diethyl diselenide (5%). With increasing temperature the yield of EtSH fell, that of thiophene remained unchanged, and no diethyl diselenide was formed. An unexpected product of this reaction was 1,2-bis(ethylthio)ethane. Its formation may be explained by bonding of EtSe radicals to diethyl disulfide to give the sulfuranyl radical-adduct **5**, which may decompose by several routes depending on the reaction conditions (scheme 12) [26]:

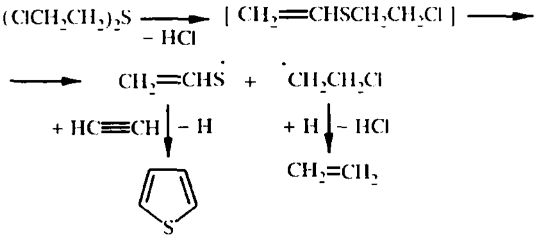
Scheme 12



At lower temperatures the EtS· radicals remove a hydrogen atom from the alkyl groups of the starting materials to yield EtSH while the more stable EtSe· radicals dimerize. At higher temperatures the radical-adduct **5** evidently disproportionates to 1,2-bis(ethylthio)ethane which facilitates complete decomposition of the diethyl selenide. In the presence of acetylene the radical-adduct **5** only generates vinylthiyl and vinylselenyl radicals which bond effectively to acetylene to give thiophene and selenophene respectively. Evidently thanks to forming an adduct **5** with Et$_2$S$_2$ the complete thermal decomposition of the EtSe· radicals is prevented. This facilitates the complete capture by acetylene of the thermal decomposition products from both diethyl selenide and diethyl disulfide.

Organo(2-chloroethyl) sulfides are effective sources of vinylthiyl radicals in gas phase thermal reactions because of the thermodynamically favorable elimination of HCl with formation of vinyl sulfides which subsequently dissociate with rupture of the C–SVin bond. For example, thiophene was formed in 45-50% yield in the co-thermolysis of bis(2-chloroethyl) sulfide with acetylene (molar ratio 1:1-3, 550-600°C) (scheme 13). Conversion of the initial (ClCH$_2$CH$_2$)$_2$S was 100% [27]. Scheme 13 was confirmed by the absence of butanethiol in the reaction products.

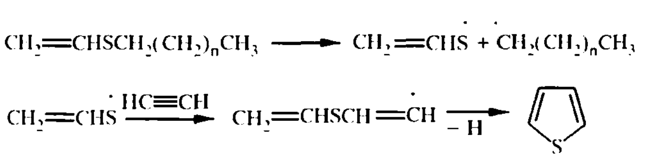
Scheme 13



Acetylene reacted analogously with ethyl 2-chloroethyl sulfide at 500-600°C. In spite of the complete sulfide conversion the yield of thiophene did not exceed 25-27%.

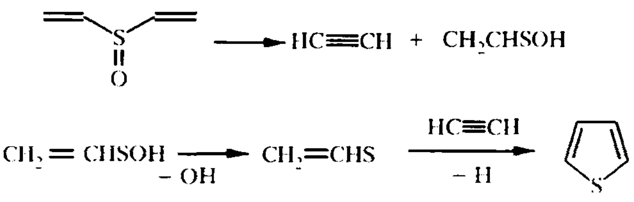
The gas phase reaction of acetylene with alkyl vinyl sulfides gave thiophene *via* formation of vinylthiyl radicals (scheme 14). The yield of thiophene reached 60-76% with butyl vinyl sulfide [27]:

Scheme 14

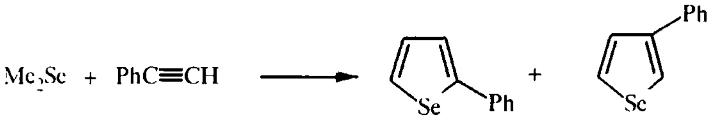


Vinylthiyl radicals and acetylene can be generated simultaneously in the gas phase from divinylsulfoxide. Its thermolysis at 400°C led to thiophene in up to 60% yield [28]. The mechanism of the reaction (scheme 15) includes a step in which the divinylsulfoxide decomposes to acetylene and vinylsulfenic acid which, in its turn, generates the HO· and CH_2=CHS· radicals. The vinylthiyl radicals then react with the acetylene:

Scheme 15

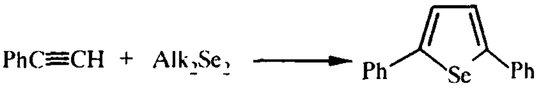


The reaction of dimethylselenide with phenylacetylene at 540°C led to 2-phenylselenophene (43% yield) together with a small amount (2%) of 3-phenylselenophene (reaction 3) [26]:



(3)

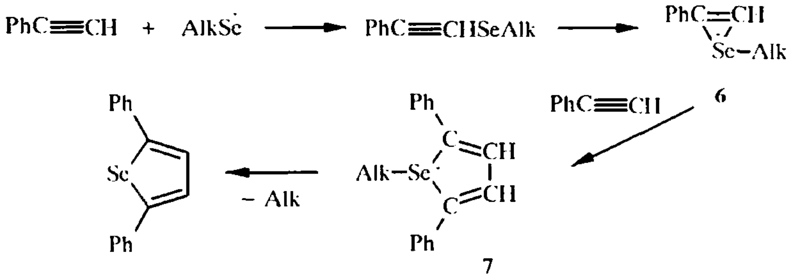
2,5-Diphenylselenophene, initially thought to have the 2,4-diphenylselenophene structure, was obtained from the liquid phase thermal reaction of phenylacetylene with dialkyldiselenides (molar ratio 2:1, 140°C) (reaction 4) [29, 30]:



(4)

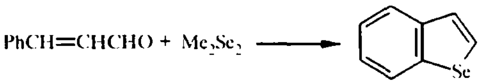
The mechanism of the 2,5-diphenylselenophene and 2,4-diphenylselenophene formation in the liquid phase reaction of phenylacetylene with dialkyldiselenides includes a stage in which vinylchalcogenyl radicals are generated and these radicals then add to the α-position of the phenylacetylene triple bond (scheme 16) [30]:

Scheme 16



The radical-adducts **6** and **7** are stabilized by loss of a hydrogen atom or an alkyl radical.

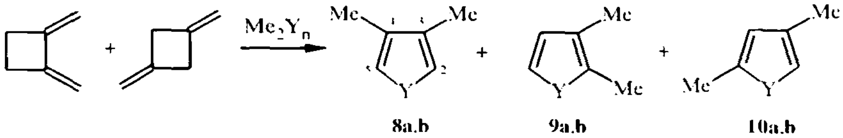
Benzoselenophene (53% yield) was the product of the gas phase reaction of Me_2Se_2 with cinnamaldehyde (molar ratio 1:1, 630°C) (reaction 5) [31, 32]:



(5)

Dimethylenecyclobutanes are specific chemical traps for allylchalcogenyl radicals.

The interaction of dimethylenecyclobutanes (a mixture of the 1,2- and 1,3-isomers) at 450-500°C with dimethylpolysulfides or dimethyldiselenide (reaction 6) gave dimethylthiophenes and dimethylselenophenes respectively as mixtures of the 3,4-, 2,3- and 2,4-isomers [33]:

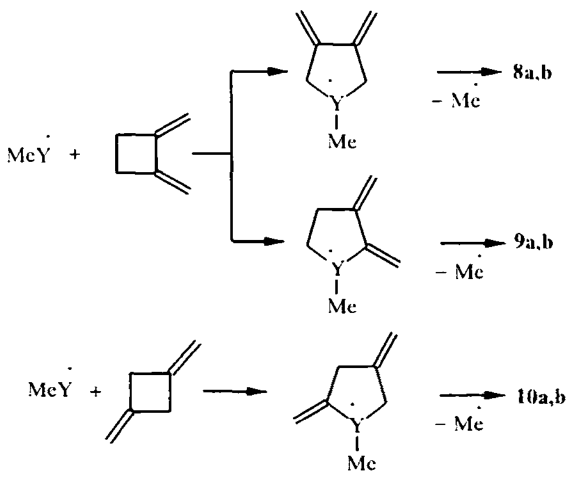


(6)

a Y = S, **b** Se: n = 2–3 (S), 2 (Se)

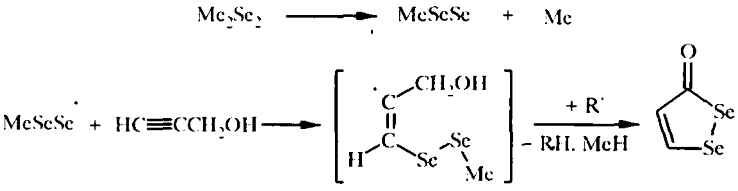
The isomeric composition is approximately the same for both dimethylchalcogenophenes: the molar ratio **8** : **9** : **10** is 3 : 1 : 1.5. The yield of dimethylthiophenes was 42%, that of dimethylselenophenes 58%. Evidently reaction (6) is initiated by the generation of chalcogenyl radicals MeY· which then break the endocyclic C–C bonds of the dimethylenecyclobutanes (scheme 17):

Scheme 17



Propargyl alcohol is an effective trap for alkylperselenyl radicals [34]. For example, the reaction of dimethyldiselenide with propargyl alcohol at 400-430°C gave 1,2-diselenol-3-one (73% yield) (scheme 18):

Scheme 18

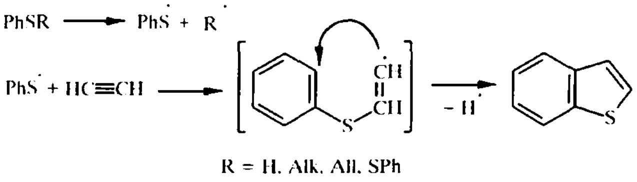


1,2-Diselenol-3-one is formed in smaller yield by the reaction of propargyl alcohol with dimethylselenide or diphenyldiselenide (25 and 16% yield respectively) [35, 36].

REACTIONS OF ARENETHIOLS AND ARYLORGANOCHALCOGENIDES

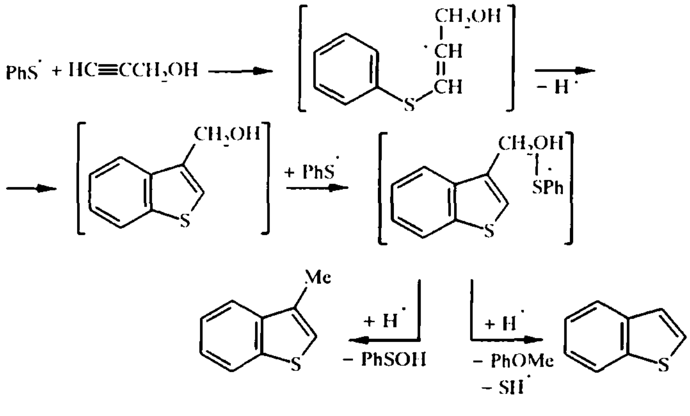
Benzothiophene (90% yield) is formed in the gas phase reaction of acetylene with thiophenol, arylalkylsulfides, or diphenyldisulfide [37, 38]. 4-Substituted thiophenols react analogously with acetylene to give 5-substituted benzothiophenes with yields of 75-95% [39]. The reaction of acetylene with 2-aminothiophenol led to 7-aminobenzothiophene [40]. These reactions occur *via* initial generation of arylthiyl radicals which then attack the triple bond of acetylene (scheme 19):

Scheme 19



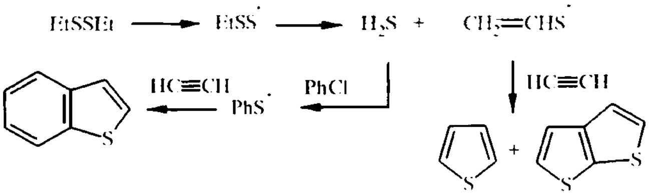
The gas phase reaction of thiophenol with propargyl alcohol at 450-630°C also gave benzothiophene in a yield of 63%. 3-Methylbenzothiophene was also formed (14%), as a result of addition of the phenylthiyl radicals to the terminal carbon atom of the triple bond of propargyl alcohol (scheme 20) [37]:

Scheme 20



Thiophenol or the phenylthiyl radicals formed from it can be generated *in situ* from hydrogen sulfide and chlorobenzene [41] or diethyldisulfide and chlorobenzene [42]. In the first case the product is benzothiophene. In the second case vinylthiyl radicals are also generated from Et_2S_2. Consequently the gas phase reaction of chlorobenzene and diethyldisulfide with acetylene at 580-700°C gave benzothiophene and thiophene, the maximum yields (34 and 44%) of which were achieved at 700°C and a ratio of chlorobenzene : Et_2S_2 : acetylene of 1 : 2 : 3. The diethyldisulfide was almost completely coupled to both chlorobenzene and acetylene to form thiophene, thienothiophene, and benzothiophene (scheme 21) [42]:

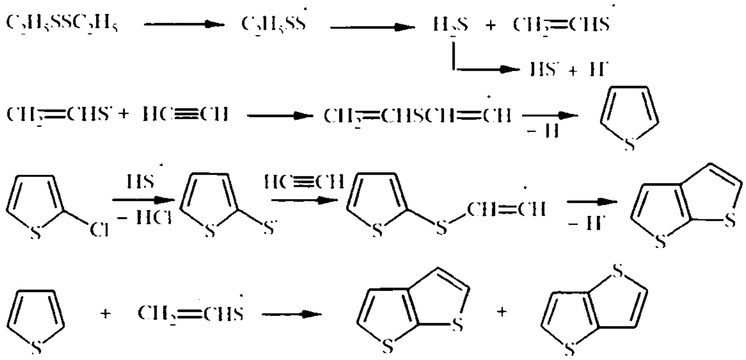
Scheme 21



The thiyl radicals HS· do not react with acetylene but replace the chlorine atom of chlorobenzene to give thiophenol. The phenylthiyl radicals generated from thiophenol react effectively with acetylene with formation of benzothiophene. Thiophene is the product of bonding vinylthiyl radicals by acetylene.

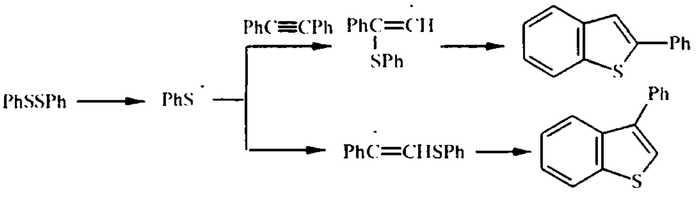
Analogous behavior was observed on the thermolysis of the Et_2S_2-acetylene-2-chlorothiophene system with a molar ratio of 1:2:3 at 500-600°C. The basic products of the reaction were thiophene (20%), thieno[2,3-*b*]-thiophene and its isomer thieno[3,2-*b*]thiophene (20%, 4:1). The products of this gas phase reaction arise from the generation of 2-thiophenethiol and thienylthiyl radicals from chlorothiophene and hydrogen sulfide, and vinylthiyl radicals from diethyldisulfide, which then react with acetylene (scheme 22), as a result of the sulfur reactant is almost completely consumed by the two substrates [41, 43, 44]:

Scheme 22



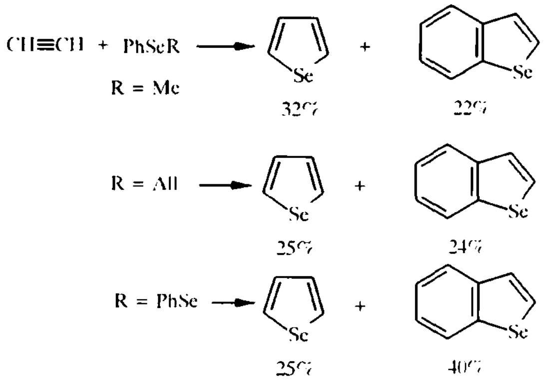
The gas phase reaction of phenylacetylene with sources of phenylthiyl radicals such as diphenyldisulfide gave 2- and 3-phenylbenzothiophenes (scheme 23) (overall yield 82% in a ratio of 1:1.5 respectively) [37]:

Scheme 23



The products of the reaction of acetylene with alkylphenylselenides at 450-500°C or with diphenyldiselenide at 500-580°C (molar ratio 1:2) were selenophene and benzoselenophene. In the first case selenophene was formed preferentially, in the second case benzoselenophene (scheme 24) [38]:

Scheme 24



GENERAL MECHANISM OF THE THERMAL REACTIONS

Thiophene and selenophene are formed in the enumerated thermal reactions *via* initial generation of two types chalcogenyl radicals from organochalcogenides or -dichalcogenides. These α,β-unsaturated (vinylchalcogenyl and arylchalcogenyl) and saturated (alkylchalcogenyl and alkylperchalcogenyl) radicals are shown in scheme 25:

Scheme 25

$$Alk_2S_2 \longrightarrow Alk\dot{S} + CH_2{=}CH\dot{S} + AlkS\dot{S}$$

$$CH_2{=}CHSAlk \longrightarrow CH_2{=}CH\dot{S}$$

$$\left.\begin{array}{l} PhSAlk \\ PhSH \\ PhSSPh \end{array}\right| \longrightarrow PhS^{\bullet}$$

$$\left.\begin{array}{l} Alk_2Se \\ Alk_2Se_2 \end{array}\right| \longrightarrow Alk\dot{S}e + CH_2{=}CH\dot{S}e + AlkSe\dot{S}e$$

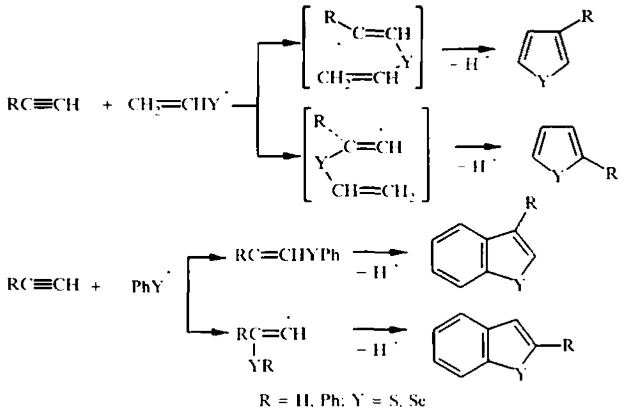
$$PhSeAlk \longrightarrow Ph\dot{S}e + Alk\dot{S}e$$

$$PhSePh \longrightarrow PhSe^{\bullet}$$

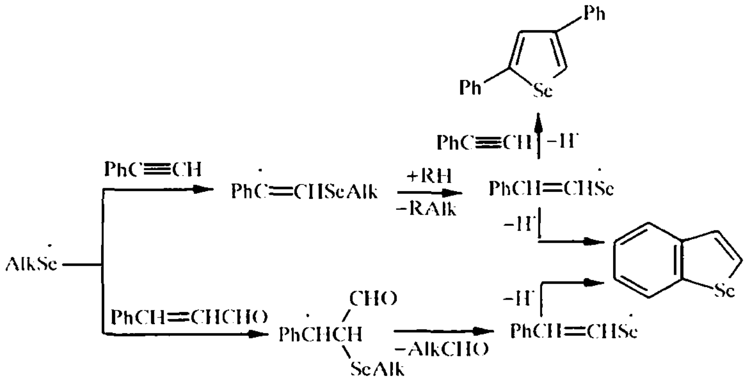
In the presence of such effective chemical traps for vinyl- and arylchalcogenyl radicals as acetylene and phenylacetylene, these radicals attack the triple bond to form radical-adducts, intramolecular condensation of which gives heterocyclic compounds (scheme 26).

The unsaturated compounds, phenylacetylene and cinnamaldehyde, with polarized multiple bonds are effective chemical traps for alkylselenyl radicals. The selenyl radicals attack the carbon atom of the multiple bond with the higher electron density to give β-phenylvinylselenyl radicals. Intramolecular cyclization of these radicals leads to benzoselenophene and condensation with phenylacetylene gives 2,4-diphenylselenophene (scheme 27).

Scheme 26



Scheme 27



The principles of the thermal reaction of hydrogen sulfide and organochalcogenides with organic compounds leads to the following necessary conditions for the formation of thiophene and selenophene rings: a 4-carbon system C=CYC=C (Y = S, Se) is formed by addition of thiyl (HS·), alkyl-, vinyl-, or arylchalcogenyl radicals to the multiple bond of unsaturated compounds, substitution by alkylselenyl radicals of functional groups at the sp^3-hybridized carbon, or opening of the strained cyclobutane ring by alkylchalcogenyl radicals. The subsequent heterocyclization of the radical-adduct occurs very rapidly.

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