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Acetylenic ethers and their analogues

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ABSTRACT. **The latest data on the chemistry of acetylenic ethers, sulphides, selenides, and tellurides are considered: their methods of synthesis, physical properties, and reactivities in relation to various reagents. The principal applications of these compounds in fine organic synthesis are indicated.**

The bibliography includes 455 references.

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I. Introduction

The vigorous development of the chemistry of acetylenic ethers and their sulphur, selenium, and tellurium analogues is associated with the high reactivity of these compounds, which makes them irreplaceable synthons in the specific synthesis of many classes of organic compounds. The principles of the chemistry of acetylenic ethers and sulphides have been examined in an exhaustive review.[1] It has been established that the regioselectivity of the addition of electrophiles and nucleophiles to acetylenic ethers can be predicted with a high degree of probability on the basis of the concept of the existence of a strong +M effect of the alkoxy-group. The mode of addition of electrophiles to acetylenic sulphides is determined by the same effect. On the other hand, the modes of addition of nucleophiles to acetylenic ethers and sulphides are different:

$$RC{\equiv}COR \xrightarrow{\overline{Nu}} R\bar{C}{=}C(Nu)OR,$$
$$RC{\equiv}CSR \xrightarrow{\overline{Nu}} RC(Nu){=}\bar{C}SR.$$

Numerous studies of the regioselectivity of the addition of various reagents to acetylenic chalcogenides, studies undertaken to determine the characteristic features of their electronic structure, and studies involving attempts to predict the regioselectivities from the standpoint of the structure–reactivity concept were published subsequently. However, the fragmentary character of the existing new reviews[2–6] precludes the assessment of the state of the problem as a whole.

The aim of the present review is the analysis of the current state of the chemistry of acetylenic ethers and their analogues and also the principal directions of its development.

II. Methods of synthesis

During the last 20 years, the existing methods of synthesis of acetylenic ethers and their analogues have been significantly improved and new procedures have been developed. The following general methods have been developed further: dehydrohalogenation of halogen-containing ethers and their analogues, the substitution of the halogen in halogenoacetylenic compounds, the reactions involving the elimination of mercaptans and alcohols, isomerisation with migration of multiple bonds, and the reactions of metal acetylides and alkali metal ethynoxides.[1]

Acetylenic ethers, sulphides, and selenides as well as their halogeno-derivatives have been obtained by the dehydrohalogenation of various saturated and ethylenic αβ- and ββ-dihalogenoethers and their analogues.[7–16]

Ethoxyethyne can be obtained particularly conveniently by the dehydrobromination of 1-bromo-2-ethoxyethene with potassium hydroxide in diglyme[17] or petroleum ether.[18,19]

The dehydrohalogenation of saturated βββ-trifluoro-substituted ethers and sulphides with the aid of lithium alkyls lengthens the hydrocarbon chain.[20] Alkylthio(seleno)ynamines $R_2NC{\equiv}CXR$ (X = S, Se) have been obtained by dehydrohalogenation with lithium dialkylamides.[21–23] The dehydrohalogenation of ββ-dichlorovinylorganyl sulphides with the aid of potassium mercaptides results in the formation of di(organylthio)acetylenes.[24,25] The dialkoxyacetylenes with an analogous structure are unstable; dimethoxyacetylene has been detected only by NMR spectroscopy in pentane at −40 °C:[26]

$$Z\text{-}CH_3OCCl{=}CHOCH_3 \xrightarrow[NH_3(liq.)]{NaNH_2} CH_3OC{\equiv}COCH_3.$$

Di-t-butoxyacetylene is the most stable; it can be stored at room temperature for several days.[27]

A vinylethynyl sulphide has been synthesised in 60% yield by the opening of the ring in 1,1-dichloro-2,2-dimethyl-3-phenylthiocyclopropane with subsequent dehydrochlorination of the 1,3-dienyl sulphide:[28,29]

$$C_6H_5SCH\text{—}C(CH_3)_2 \xrightarrow{(CH_2)_3COK} C_6H_5SCH{=}CClC(CH_3){=}CH_2 \xrightarrow{-HCl}$$
$$\xrightarrow{-HCl} C_6H_5SC{\equiv}CC(CH_3){=}CH_2.$$

A series of diacetylenic sulphides have been synthesised by the dechlorination of chlorine-containing 1,3-dienyl or vinylethynyl sulphides:[30]

$$RSCCl{=}CClCCl{=}CCl_2 \xrightarrow[-70\ ^\circ C]{C_4H_9Li} RSC{\equiv}CC{\equiv}CLi \xrightarrow{R^1Hal} RSC{\equiv}CC{\equiv}CR^1,$$

R = cycloalkyl, Ph; R^1 = H, $(CH_3)_3Si$, $(C_6H_5)_3Sn$, organyl.

A method of synthesis of an ethynyl vinyl sulphide has been developed:[31]

$$(CH_3)_3SiC{\equiv}CSCH_2CH_2Cl \xrightarrow[NH_3(liq.)]{LiNH_2} LiC{\equiv}CSCH{=}CH_2 \xrightarrow{H_2O} HC{\equiv}CSCH{=}CH_2.$$

Phenylethynyl ethers have been obtained in a low yield from phenylethynyl halides on treatment with alkoxides:[32,33]

$$C_6H_5C{\equiv}CX \xrightarrow{RONa} C_6H_5C{\equiv}COR,$$
$$X = Cl, Br;\quad R = alkyl.$$

A reaction mechanism, including addition, β-elimination and sulphenium ion formation stages, has been proposed as a result of a study of the nucleophilic substitution of chlorine in t-butylchloroacetylene by the thiophenoxide ion.[34,35] The rate constants for the substitution of a halogen[36] are correlated with Charton's steric constants of the alkylthio-groups σ_{SR}.[37]

Substituted acetylenic ethers,[38,39] sulphides,[38,41] and selenides[40,41] as well as ethynyl vinyl sulphides[42,43] have been obtained from the corresponding acetylenic halides by a similar procedure.

A two-stage method of synthesis of terminal ethynyl sulphides has been developed. It is based on the reaction of chloroethynyldimethylcarbinol with alkali metal thiolates and subsequent cleavage of the resulting dimethyl(organylthioethynyl)carbinol by heating with potassium hydroxide.[3,44–46] Terminal acetylenic ethers have been obtained similarly but in low yields.[47,48]

Halogen-containing acetylenic ethers and sulphides enter into the reaction involving the nucleophilic substitution of the halogen on treatment with organometallic compounds:[3,24,49–51]

$$RZC{\equiv}CX + R^1M \rightarrow RZC{\equiv}CR^1 + MX,$$
$$Z{=}O: R{=}C_2H_5;\ X{=}I;\ R^1{=}Ar;\ M{=}Cu{\cdot}MgBr_2;$$
$$Z{=}S: R = alkyl,\ C_6H_5;\ X = Cl, Br;\ R^1 = organyl;$$
$$N(C_2H_5)_2;\ M{=}Li,\ Cu{\cdot}MgX_2.$$

Chloroethynyl organyl sulphides react with mercaptoethanol in the presence of potassium hydroxide to form di(organylthio)-acetylenes.[52] The reactions with secondary amines have afforded organylthioynamines,[14,53,54] while those with tertiary amines and phosphines gave rise to ammonium and phosphonium salts:[14,15,55]

$$RSC{=}CCl \xrightarrow{HNR^1_2} RSC{\equiv}CNR^1_2,$$
$$R = alkyl;\ R^1_2N = morpholinyl, piperidinyl, piperazinyl.$$

$$[RSC{\equiv}CP(C_2H_5)_3]^+Cl^- \xleftarrow{(C_6H_5)_3P} RSC{\equiv}CCl \xrightarrow{R^1_3N} [RSC{\equiv}CNR^1_3]^+Cl^-,$$
$$R,\ R^1 = alkyl.$$

Trialkyl phosphites react with chloroethynyl organyl sulphides in accordance with the mechanism of the Arbuzov rearrangement to form organylthioethynylphosphonates:[15,56]

$$RSC{\equiv}CCl + P(OR^1)_3 \rightarrow RSC{\equiv}CP(O)(OR^1)_2 + R^1Cl;\ R,\ R^1 = alkyl.$$

The 1,4-elimination of a mercaptan from 1,4-dialkyl- or 1,4-di(phenylthio)but-2-ynes on treatment with potassium alkoxide in liquid ammonia by a standard procedure[1] led to high yields of vinylethynyl sulphides.[57] When an attempt was made to synthesise a vinylethynyl ether from 1,4-dialkoxybut-2-yne, ethynyl vinyl ether or a butatrienyl ether were obtained.[58] Vinylethynyl ethers were synthesised by treating compound (I) with ethyllithium:[59]

$$ROCH{=}C{=}CHCR^1R^2OR \xrightarrow{C_2H_5Li} ROC{\equiv}CCH{=}CR^1R^2,$$
(I)

$$R = alkyl;\ R^1, R^2 = H, alkyl, cyclopentyl.$$

A mixture of ethynyl and 1,3-dienyl sulphides was obtained by the isomerisation of 1-t-butylthiobuta-2,3-diene in the presence of sodium ethoxide in alcohol.[60] The study of the kinetics of the isomerisation of propargyl selenides to methylethynyl selenides established the carbanionic nature of the intermediate compound.[61]

The isomerisation of allenic sulphides to acetylenic sulphides can be induced by catalytic amounts of an amine or on heating.[62] During the formation of propargyl sulphides, their isomerisation to allenic and acetylenic sulphides is frequently observed.[63]

Metal acetylides have found extensive application as the starting materials for the synthesis of acetylenic sulphides and their analogues. An ethynyl sulphide has been obtained by refluxing copper phenylacetylide with 4,6,8-trimethyl-1-thiocyanato-azulene in dimethylformamide (DMF).[64] The Iotsich reagent reacts with arenesulphenyl chloride to form acetylenic sulphides.[65] Acetylenic selenides have been obtained by the reaction of silver[66] or lithium[67] acetylide with benzene selenyl bromide. Arylethynyl tellurides have been prepared by treating metal acetylides with arene-tellurenyl halides.[68,69]

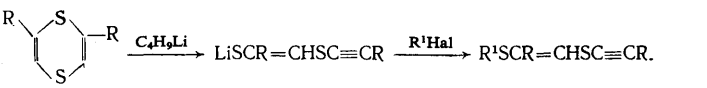
The reaction of lithium acetylide with α-bromodithioisobutyric acid ester leads to the formation of an ethynyl sulphide:[70]

$$(CH_3)_3CC{\equiv}CLi + (CH_3)_2CBrC(S)SCH_3 \rightarrow$$
$$\rightarrow (CH_3)_3CC{\equiv}CSC(SCH_3){=}C(CH_3)_2 + LiBr.$$

The first[1] and a series of subsequent attempts at the synthesis of ethynyl ethers from lithium alkylethynoxide[71] or an acetylenic potassium dithiolate,[72,73] by treating them with alkyl halides were unsuccessful. However, the reaction of lithium alkylethynoxide with trialkylsilyl chloride[74] or diethyl phosphorochloridite[75] leads to the formation of the corresponding ethynyl ethers.

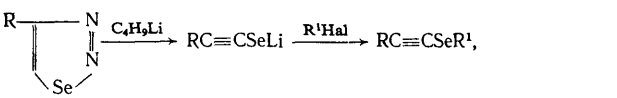
The simplest method of synthesis of ethynyl sulphides and their analogues became the reaction of a metal acetylide with the chalcogen and subsequent alkylation of the metal thiolate.[1] The methods of synthesis of acetylenic alkali metal thiolates have been published in reviews[76,77] and their use for the synthesis of ethynyl sulphides and their analogues has been described in a monograph.[78] A series of ethynyl sulphides,[3,79–84] selenides, and tellurides[41,69,85–87] have been obtained by this method. Dialkyl thiosulphonates have been used as alkylating agents for the synthesis of asymmetric di(alkylthio)acetylenes.[88] Acetylenic lithium thiolate has been used in an especially great variety of ways as the reagent for the synthesis of ethynyl sulphides.[89–98]

Ethynyl sulphides have also been obtained by treating 1,4-dithiines with butyllithium:[99]



$$R = H, alkyl;\ R^1 = alkyl.$$

Acetylenic lithium selenolates are obtained by treating substituted selenodiazoles with butyllithium:[100]



$$R = alkyl, aryl;\ R^1 = alkyl.$$

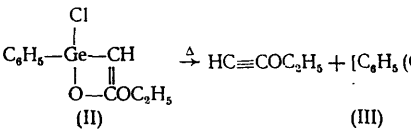
Acetylenic alkali metal thiolates (selenolates, tellurolates), which are ambient anions, enter into reactions involving the anionic 1,3-cycloaddition and nucleophilic addition to the triple bond, apart from the nucleophilic substitution of the metal.[100,101] Ethynyl selenides[100,102,103] and tellurides[100] are therefore frequently formed in a mixture with heterocyclic compounds.

Acetylenic potassium selenolates react with epichlorohydrin to substitute the chlorine atom or to cleave the epoxide ring.[104]

An ethynyl telluride has been obtained by oxidising sodium phenylethynyltellurolate with iodine:[105]

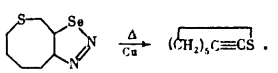
$$2C_6H_5C{\equiv}CTeNa \xrightarrow[-NaI]{I_2} [C_6H_5C{\equiv}CTeTeC{\equiv}CC_6H_5] \xrightarrow{-Te} \rightarrow C_6H_5C{\equiv}CTeC{\equiv}CC_6H_5.$$

A new aspect of the methods of synthesis of acetylenic ethers and their analogues is thermosynthesis. Thus ethoxyacetylene and a germoxane (III) have been obtained in 25–30% yield by the decomposition of the unstable compound (II):[106]



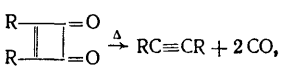
(II) (III)

1-Thiacyclooct-2-yne (V) was synthesised for the first time in 15% yield by heating compound (IV) in the presence of copper:[107]



(IV) (V)

Acetylenes have been obtained by the thermal decomposition of 3,4-di(methylthio)- or 3,4-di(methylseleno)cyclobutene-1,2-diones:[108]



R = CH_3S, CH_3Se.

Di(ethylthio)acetylene has been synthesised in 53% yield by the thermolysis of the phosphorylide (VI):[109]

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}=C(SC_2H_5)_2 \xrightarrow{\Delta} C_2H_5SC{\equiv}CSC_2H_5.$$

(VI)

The thermolysis of the phosphorylides (VII) afforded internal ethynyl selenides:[110]

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(SeAr)COR \xrightarrow{\Delta} RC{\equiv}CSeAr,$$

(VII)

R = alkyl, aryl.

Terminal ethynyl ethers and sulphides can be readily converted into the corresponding internal compounds by the substitution of the terminal hydrogen atom by metals. Thus various element-containing and functional derivatives of a metal-substituted ethoxyacetylene have been obtained from the latter:

$$C_2H_5OC{\equiv}CM \xrightarrow{RHal} C_2H_5OC{\equiv}CR,$$

M = Li, MgBr; R = CH_3CO (Ref.111), Alk_2P, Ar_2P (Refs.112, 113), $(CH_3)_3Si$ (Ref.2), $(CH_3)_2C_6H_5Si$ (Ref.114), Alk_3Ge, Alk_3Sn (Ref.6).

Lithium ethoxyethynylboranate has been synthesised by treating lithium ethoxyacetylide with a trialkylborane. Treatment of the boranate with iodine led to the synthesis of internal ethynyl ethers in 30–58% yields:[115,116]

$$R_3B + LiC{\equiv}COC_2H_5 \xrightarrow[THF]{0°C} Li^+R_3\overline{B}C{\equiv}COC_2H_5 \xrightarrow{I_2} RC{\equiv}COC_2H_5,$$

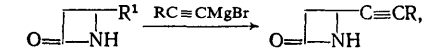
R = C_4H_9, $C_2H_5CHCH_3$.

The interaction of lithium ethoxyacetylide with epoxyethane or epoxypropane gave rise for the first time to vinylethynyl ethers.[117]

The reaction of dialkylamino(trialkyl)stannanes with ethoxyacetylene is a convenient method of synthesis of tin-containing ethynyl ethers.[6]

Phosphorus-containing ethynyl sulphides have been obtained from a methylthioacetylenic Iotsich reagent and phosphinic acid chlorides.[118]

The reaction of ethoxy- or phenylthio-ethynylmagnesium bromide with 4-benzenesulphonyl- or acetoxy-azetidine has been used to synthesise a heterocyclic ethynyl ether and sulphide:[119]



R = C_2H_5O, C_6H_5S; R^1 = $C_6H_5SO_2$, CH_3COO.

Alkynyl carboxylates and phosphates (X) have been obtained for the first time from the iodonium salts (VIII) by an ion-exchange reaction in the presence of an ion-exchange resin saturated with the anion A^-.[75] In contrast to compounds (IX, A = $OCOR^1$), compounds [IX, A = $OP(O)(OC_2H_5)_2$] are stable crystalline substances:

$$[RC{\equiv}ClPh]^+Ts^- \xrightarrow{A^-} [RC{\equiv}ClPh]^+A^- \rightarrow RC{\equiv}CA + PhI,$$

(VIII) (IX) (X)

A = $OCOR^1$, $OP(O)(OC_2H_5)_2$; R = alkyl, R^1 = aryl.

III. Physical properties

The electronic structure of ethynyl ethers and their analogues has been investigated by various physical methods. Previously published studies involving the analysis of the dipole moments (d.m.) of ethynyl sulphides and ethers did not provide unambiguous data about the direction of polarisation of the triple bond in the $-C{\equiv}C-S-$ system.[1]

As a result of the investigation of the dipole moments of phenylethynyl sulphides and their analogues p-$YC_6H_4XC{\equiv}CR$ (R = H, C_6H_5; X = S, Se, Te; Y = H, CH_3, Cl, Br, CH_3O, NO_2), new studies led to the discovery of the dependence of the direction of polarisation of the triple bond on the character of the substituents at the heteroatom and at the triple bond.[120–130] It was shown that, in the case of electron-donating substituents, the sulphur, selenium, and tellurium atoms behave as π-donors in relation to the triple bond, which increases the $X-C_{sp}$ bond order. The character of the polarisation of the triple bond is the same in this case: $-XC^{\delta+}=C^{\delta-}-$. An electron-accepting substituent (Y = NO_2) reverses the direction of polarisation of the triple bond. The occurrence of direct conjugation in the $-XC{\equiv}CC_6H_4Y$ group with the varied substituent (Y) via the benzene ring with inversion of the direction of the shift of electron density in the triple bond on passing from Y = CH_3O to Y = NO_2 was established.

The dependence of the dipole moments of ethynyl sulphides on the induction constants of the ethynyl[81] and alkyl groups at the heteroatoms[131] confirms the high sensitivity of the $-C{\equiv}CX$-system to the influence of substituents.

The influence of Group VIA heteroatoms at the triple bond on the degrees of shielding of the carbon atoms is clearly manifested in the ^{13}C NMR spectra. The inversion of the relative shielding of the α- and β-carbon atoms of the triple bond on passing from ethers to sulphides has been adopted as evidence for the manifestation of the $-M$ effect by the alkylthio-group in contrast to the alkoxy-group.[132,133] The shielding of the α-carbon atoms and the deshielding of the β-carbon atoms increase linearly with decrease in the electronic activity of the heteroatom in the series of ethynyl chalcogenides.[134,135]

Correlation analysis of the ^{13}C NMR spectra of acetylenic compounds established the additivity of the contribution of the substituents to the chemical shifts of the carbon atoms of the triple bond. The effects of the substituents constitute a linear combination of their induction, resonance, and steric constants.[136,137]

The study of the NMR spectra of ethoxyacetylene[138] and silicon-, germanium-, and tin-containing ethynyl ethers[139–141] and sulphides[142] showed that the alkoxy-group is an effective *p*-donor in relation to the triple bond, while the alkylthio-group is a weak *p*-acceptor.[143] However, the deshielding of the tellurium atom in 1-methyltellurobut-3-en-1-yne compared with dimethyl telluride, established from the ^{125}Te NMR spectra,[144] may be a consequence of a weak electron-donating effect of the methyltelluro-group in relation to the triple bond.

The $^{77}Se-^{13}C$ spin–spin coupling constants (SSCC) of ethynyl selenides have been measured and the influence of the medium on the shielding of the ^{77}Se atoms has been investigated.[145–147]

The carbon atoms of the triple bond in di(ethylthio)acetylene are deshielded compared with the terminal ethynyl sulphides.[148]

An equation which simplifies the assignment of the signals of the carbon atoms of the triple bond in ethynyl sulphides and their analogues has been proposed.[149]

The intensity of the band due to the triple bond in the Raman spectrum of t-butylthioacetylene is approximately twice as great as in the spectrum of butylacetylene, which is evidence of an effect of the conjugation of the triple bond with the alkylthio-group.[150,151] The stretching vibration frequencies of the triple bond in the Raman spectra of phenylethynyl sulphides and their analogues, $CH_3XC{\equiv}CC_6H_5$ and $p\text{-}YC_6H_4XC{\equiv}CC_6H_5$ (X = S, Se, Te; Y = H, CH_3, CH_3O, F, Cl, Br, NO_2), decrease in the sequence S > Se > Te, whilst their integral intensities increase. It has been concluded that the sulphur and selenium atoms participate in the transmission of conjugation via the triple bond. In relation to tellurides, a distinct manifestation of this effect has not been observed.[126,152]

The intensity of the absorption bands of the triple bond in the IR spectra of ethoxy- and ethylthio-acetylenes is determined by the resonance interaction with the substituent. It has been shown that the sulphur atom in the molecules of methylthiophenylacetylene and 1-ethylthio-3,3-dimethylbut-1-yne is involved in conjugation with both π-bonds of the acetylenic fragment.[153] The integral intensities of the triple bond in ethoxy- and phenoxy-acetylenes are not correlated with the induction constants of the substituents.[154]

The force constants of the bonds in the molecules of methoxyacetylene and trimethylsilylmethoxyacetylene have been calculated.[155,156] The absorption bands in the IR spectrum of methylthioacetylene have been assigned.[151]

A combined study of the IR, UV, and NMR spectra of silicon-, germanium-, and tin-containing ethynyl ethers and sulphides demonstrated the occurrence of interaction via the triple bond.[143,157] It has been established that the intensity of the absorption bands of the triple bond in the IR spectra of structurally similar germanium- and tin- containing compounds depends on the inductive effect of the substituents. In the case of silicon-containing compounds, there is in addition the influence of the specific interaction of the silicon atom with the triple bond.

The possibility of an approximate quantum-mechanical approach to the description of the behaviour of the stretching vibration frequencies of the $C_{sp}-H$ bond in methoxyacetylene has been examined.[158]

Apart from the absorption bands assigned to the $\pi \rightarrow \pi^*$ electronic transition, the UV spectra of vinyl- and phenyl-ethynyl sulphides and their analogues contain a band which has been assigned to the $n \rightarrow \pi^*$ transition, the band being most pronounced in the spectra of the tellurides.[126,159–161] Analysis of the UV spectra indicates an increase in the degree of interaction of the heteroatoms with the triple bond in the electronically excited state in the direction Te < Se < S, which is the opposite of the direction of variation in the ground state. This interaction can be attributed to the variation of the ionisation potentials, diminishing on passing to the tellurides, which promotes charge transfer to the triple bond in the excited state. The ionisation potentials of ethynyl sulphides have been obtained in the study of the mass spectra[162,163] and those of the sulphides and selenides have been determined by the method of photoelectron ionisation.[108,164] The ionisation potentials of di(methylthio)acetylene have been calculated by the MNDO method.[165]

The photoelectron spectra of 1-ethoxybut-3-en-1-yne[166] and ethynyl sulphides have been obtained.[167] Radicals have been detected in the laser photoionisation of the deuterium-containing di(methylthio)acetylene[168] and a radical-cation has been detected in the radiation-induced ionisation of methoxyacetylene.[169]

The decrease in the $C_{sp}-X$ bond length in methoxyacetylene,[170,171] ethoxyacetylene,[172] and methylthio-[173] and ethylthio-acetylenes,[174] established by microwave spectroscopy, may be a consequence of the effect of p,π conjugation. The potential energy of the internal rotation of the methylthio-group in methylthioacetylene is higher than that of the methoxy-group in methoxyacetylene,[175] which has not so far been satisfactorily explained. The microwave spectrum of ethoxyacetylene has been used in a computer program for the identification of the radiospectra of the molecular clouds in space.[176]

It has been established by gas electron diffraction that the di(methylthio)acetylene molecule exists preferentially as the conformer with a CSSC dihedral angle of 86°.[148]

The study of the X-ray fluorescence *K* spectra of sulphur in aryl and pentafluorophenylethynyl sulphides established that the *d* orbitals of sulphur are appreciably populated with retention of the p,π conjugation effects.[65]

The formation energies of methoxy- and methylthio-acetylenes,[177] the geometrical parameters of methoxyacetylene,[178] the distribution of electron density,[179] and the stabilisation energy[180,181] have been calculated by quantum-chemical methods.

Thus the triple bond in ethynyl sulphides and their analogues differs from that in the ethynyl ethers by an increased sensitivity to the influence of substituents associated with the possibility of the manifestation of the effect of d,π interaction by the heteroatoms.

The differences between the electronic structures of ethynyl ethers and their analogues are manifested by the greater acidity of the terminal ethynyl sulphides compared with the ethers and acetylenic hydrocarbons.[150,182] A linear relation between the kinetic and thermodynamic CH acidities of ethynyl ethers or sulphides has been established.[183] The state of the exchange equilibrium in the ethoxyacetylene–*p*-fluorophenylethynylcyclohexylmercury has been investigated by ^{19}F and ^{1}H NMR.[184] The stabilisation energy of methoxyacetylene in the reaction involving the exchange of the methoxy-group has been calculated by the quantum-chemical method.[185]

The formation of hydrogen bonds in aryloxyacetylenes has been investigated by IR spectroscopy.[186] It has been shown that the basicity of ethoxyacetylene in the interaction with phenol depends on the inductive effect of the ethoxy-group.[187] The energy of the hydrogen bond between phenol and vinylethynyl sulphides, selenides, and tellurides increases on passing to the tellurides[188] in parallel with

the energy of the electronic excitation of the molecules. The oxygen or sulphur atom is the centre involved in the hydrogen bond with phenol in the molecules of silicon-, germanium-, and tin-containing ethynyl ethers and sulphides.[157]

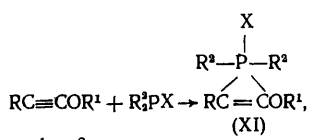
The antiparallel variation of the electronic structure of the molecules in the series of ethynyl ethers and their analogues with their susceptibility to the perturbing effect of reagents is manifested by the regioselectivity of the addition of the reagents to the triple bond in ethynyl sulphides.

IV. Chemical properties

1. The addition of electrophiles

It was established previously that the addition of electrophiles to ethynyl ethers and sulphides takes place with the attachment of the electrophilic component of the reagent to the β-carbon atom of the triple bond.[1] The addition of phosphorus pentachloride, phosphorus trihalides, dialkylhalogenophosphines, dialkyl phosphorohalidites, mercury chloride, Group IV element tetrachlorides, and trialkylstannyl chloride to ethynyl ethers proceeds in accordance with this rule.[2,6,189–195] Asymmetric di(alkylthio)- and di(arylthio)-acetylenes react with phosphorus pentachloride to form equal amounts of regioisomers.[196,197] Ethynyl sulphides react with phosphorus tribromide similarly to the ethers.[198] The reaction of 3-t-butyl-1-ethoxy-3-methylprop-1-yn-3-ol with phosphorus trichloride in the presence of pyridine leads to the formation of ethyl 2-dichlorophosphino-3,4,4-trimethylpent-2-enoic acid.[199]

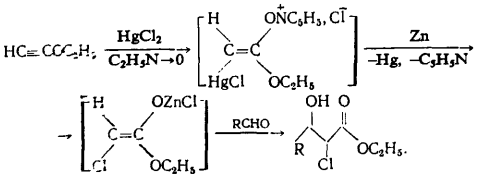
In the absence of a catalyst, new representatives of phosphirenes (XI) are formed in almost quantitative yields from dialkyl and diaryl-halogenophosphines by the reaction with internal ethynyl ethers:[200]



(XI)

R, R^1, R^2 = alkyl, aryl; X = Cl, Br.

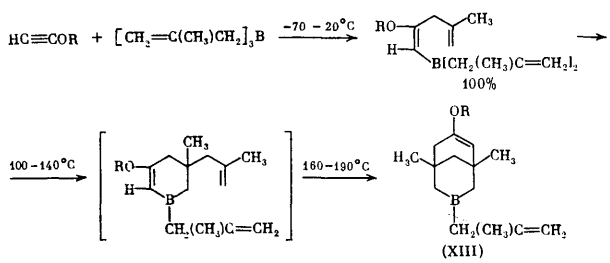
The successive treatment of ethoxyacetylene with mercury chloride, pyridine *N*-oxide, and zinc dust leads to the formation of the enolate (XII), which reacts with aldehydes to form α-chloro-β-hydroxyesters:[201]



(XII)

Triethylsilane reacts with phenoxyacetylene in the presence of a modified Speier catalyst predominantly with attachment of the triethylsilyl group to the β-carbon atom of the triple bond.[202] Triethylgermane reacts at the triple bond under similar conditions with 90% regioselectivity, forming a 1 : 1 mixture of the (*Z*)- and (*E*)-isomers.[203]

Boron-containing reagents, which we have formally classified as electrophilic, add to terminal ethynyl ethers with attachment of the boron atom to the β-carbon atom of the triple bond and the formation of ethylenic boranes. Thus the hydroboration of ethoxyacetylene[204,205] leads to the formation of tri(*trans*-2-ethoxyvinyl)-borane. The mode of addition of dialkyl- and triorganyl-boranes to ethoxyacetylene is similar.[204–209] The stereoselectivity of the addition of dialkylboranes to ethynyl selenides with subsequent acidolysis of the intermediate has been used to synthesise (*Z*)-vinyl selenide.[110,210,211] (*Z*)-β-Trimethylsilylvinyl ether has been obtained by the same method.[212] The allylboration of alkoxyacetylene proceeds stereoselectively as *cis*-addition.[213–215] Heating of the adduct leads to the allyl rearrangement with formation of the bicyclic borane (XIII):

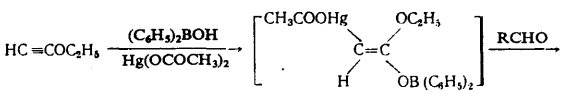


(XIII)

R = alkyl.

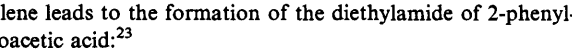
The use of the products of the addition of allylboranes to ethynyl ethers as synthons has been the basis of a method of synthesis of other unsaturated compounds. Thus 2-alkoxypenta-1,4-dienes have been synthesised[217] by the alcoholysis of the products of the addition of dialkylallylboranes to ethynyl ethers.[216] The addition of triallylborane to ethoxyacetylene and subsequent treatment of the products with triethylaluminium led to the synthesis of pent-1-en-4-yne.[218] The regioselectivity of the addition of the dialkylborylmethylcyclobut-1-ene–dialkylboryl-2-methylene-cyclobutane system is similar to the regioselectivity of the addition of allylboranes.[207]

Ethoxyacetylene reacts with aldehydes in the presence of diphenylboronic acid and mercury acetate with formation of approximately equal amounts of β-hydroxy- and β-acetoxy-esters.[219] The coupled addition of diphenylboronic acid and mercury acetate to ethoxyacetylene apparently takes place initially:



R = alkyl, aryl.

The study of the mechanism[3] and regioselectivity of the hydration reactions of internal ethynyl ethers and their analogues has been continued. Thus the hydration of diethylaminophenylselenoacetylene leads to the formation of the diethylamide of 2-phenylselenoacetic acid:[23]



The mode of hydration of 4,4-dichloro-1-methoxybut-1-yn-3-one[220] and 1-alkylselenobut-3-en-1-ynones[85] is similar to the familiar hydration reaction of ethynyl ethers.[1]

The product of the addition of two alcohol molecules to ethoxyacetylene can be used as a plasticiser of solid polymers.[221] Phenols react with ethoxyacetylene regiospecifically with formation of α-aryloxyvinyl ethers.[222]

The bromination of ethoxyacetylene[223] and phenoxyacetylene[224] leads to the formation of di- and tetra-bromides. The halogenation of vinylethynyl sulphides and selenides involves predominantly the triple bond.[225,226] The tetrabromide has been obtained by the

bromination of 1-methyltellurobut-3-en-1-yne as a result of the addition of bromine to the double bond and to the tellurium atom.[227]

The joint chlorination of ethoxyacetylene and epoxyethane afforded a chlorine-containing orthoester:[228]

$$HC{\equiv}COC_2H_5 + 2\,Cl_2 + 2\,CH_2{-}CH_2 \rightarrow CHCl_2C(OCH_2CH_2Cl)_2(OC_2H_5).$$
$$\qquad\qquad\qquad\qquad\qquad\quad \backslash O /$$

The interaction of ethynyl ethers with sulphur monochloride pentafluoride proceeds with substitution of the alkoxy-group and the formation of 2,2-difluoro-1-pentafluorothioethylene.[229]

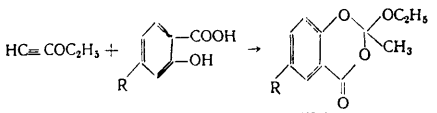
The hydrohalogenation of substituted ethynyl ethers[230] and sulphides[118] is regioselective[1] and proceeds in accordance with the *trans*-addition rule. The hydrochlorination of di(alkylthio)- and di(alkylseleno)-acetylenes proceeds predominantly as *trans*-addition with 80% regioselectivity for asymmetric di(alkylthio)acetylenes.[231] Vinylethynyl selenides combine with hydrogen chloride selectively via the triple bond:[232]

$$CH_2{=}CHC{\equiv}CSeR \xrightarrow{HCl} CH_2{=}CHCH{=}C(Cl)SeR,$$
$$R = \text{alkyl}.$$

The bond between the acetylenic carbon atom and tellurium in vinylethynyl tellurides is cleaved on treatment with hydrogen chloride.[232] The hydrochlorination of a diethynyl sulphide[233] and selenide[234] afforded only the 1,3-diene products of the addition of two molecules of hydrogen chloride: $C_2H_5CH{=}CClCH{=}CClXCH_3$ (X = S, Se). Calculation by the CINDO/2 method of the perturbation energy of the hydrochlorination reaction of vinylethynyl sulphides and selenides in an ionising solvent has led to the conclusion that the reaction is subject to orbital control.[234]

The mode of addition of carboxylic acids to ethynyl ethers[224,235–239] is of the usual type.[1] Acid anhydrides are formed from trimethylsilylethoxyacetylene by reaction with carboxylic acids.[240]

Ethoxyacetylene and 5-(4-fluorophenyl)salicylic acid react to form the benzodioxane (XIV), which has analgesic properties:[241]



(XIV)

$R = p\text{-}FC_6H_4.$

Certain products of the addition of carboxylic acids exhibit chemiluminescence[239,242] or can be recommended as UV-stabilisers of polymers.[238]

Alkanesulphonic acids in the form of pyridinium salts add to ethoxyacetylene with the usual mode of addition of the acid residue.[243]

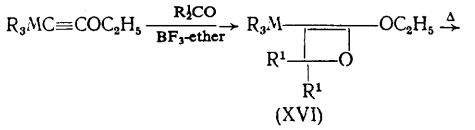
Fluorosulphonic acid adds to the ethoxyacetylene regiospecifically with formation of compound (XV):[244]

$$HC{\equiv}COC_2H_5 \xrightarrow[SO_2ClF,\ -60\ ^\circ C]{FSO_3H} CH_2{=}C(OC_2H_5)OSO_2F.$$
(XV)

Like the analogous ethynyl ethers, ethynyl sulphides[3] and vinylethynyl sulphides,[245] selenides,[246] and tellurides[188] combine with carboxylic acids chemoselectively via the triple bond with the usual mode of addition of the acid residue. On being refluxed in acetic acid, 1-methyltellurobut-3-en-1-yne is protodemetallated with formation of vinylacetylene. Di(alkylthio)acetylenes react with carboxylic acids to form predominantly the (*E*)-isomers of vinyl sulphides.[247]

Methanesulphenyl chloride adds to vinylethynyl sulphides at the triple bond with formation of 1-chloro-2-methylthiobutadienyl sulphides.[248]

One of the methods of synthesis of αβ-unsaturated acid esters is the reaction of ethynyl ethers with carbonyl compounds in the presence of boron trifluoride etherate.[249–252] Substituted oxetenes (XVI) are sometimes formed, isomerising on heating:



(XVI)

$$\rightarrow (CX)_2C{=}C(MR_3)COOC_2H_5,$$
$$M = Si, Ge;\ R^1 = CF_3,\ CF_2Cl,\ \text{alkyl};\ R = \text{alkyl},$$
$$R_3M = H,\ R^1 = CF_3,\ CF_2NO_2.$$

In the absence of the catalyst, trimethylstannylethoxyacetylene adds to ketones, the adduct isomerising to an α-stannylated acrylate after the addition of a catalyst:[250]

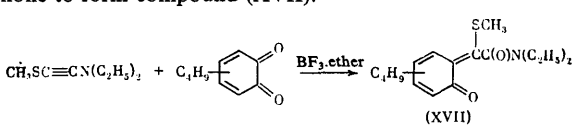
$$(CH_3)_3SnC{\equiv}COC_2H_5 \xrightarrow{(CF_2Cl)_2CO} (CF_2Cl)_2C[OSn(CH_3)_3]C{\equiv}$$
$$\equiv COC_2H_5 \xrightarrow{BF_3\text{.ether}} (CF_2Cl)_2C{=}CSn(CH_3)_3COOC_2H_5.$$

The reaction of diisopropylaminophenylselenoacetylene with perfluoroacetone leads to the formation of the amide of an αβ-unsaturated acid.[23]

$$(iso\text{-}C_3H_7)_2NC{\equiv}CSeC_6H_5 \xrightarrow[BF_3\text{.ether}]{(CF_3)_2CO} (CF_3)_2C_2{=}C(SeC_6H_5)CON(iso\text{-}C_3H_7)_2.$$

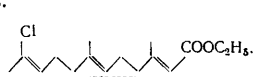
Phosgene[253] and acetyl chloride[254] add to internal ethynyl ethers with formation of α-chlorovinyl ethers.

Diethylamino(methylthio)acetylene reacts with a substituted *o*-quinone to form compound (XVII):[51]



(XVII)

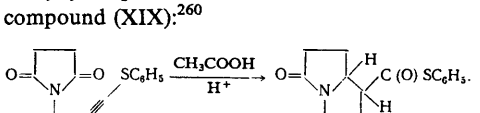
Ethoxyacetylene has been used in the synthesis of αβ-unsaturated esters,[255–257] among which compounds of type (XVIII) are juvenile-hormonal insecticides:[258]



(XVIII)

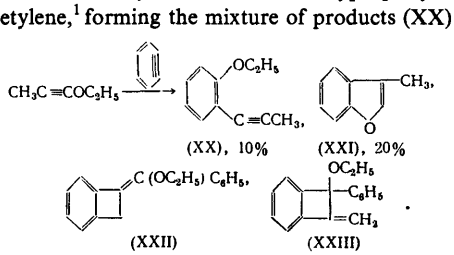
The reaction of terminal ethynyl sulphides with thiophenaldehydes afford esters of αβ-unsaturated thio-acids.[259]

The intramolecular addition of the carbonyl group to the triple bond of an ethynyl sulphide in an acid medium leads to the formation of compound (XIX):[260]



(XIX)

Dehydrobenzene readily reacts with 1-ethoxyprop-1-yne[261] as well as ethoxyacetylene,[1] forming the mixture of products (XX)–(XXIII):



(XX), 10% (XXI), 20%

(XXII) (XXIII)

The main product of the reaction of dehydrobenzene with ethylthioacetylene is benzothiophen.[261]

2. The addition of nucleophiles

The previously established different modes of addition of nucleophiles to ethynyl ethers and sulphides are usually interpreted from the standpoint of the concept of the mesomeric stabilisation of cryptoanions by the sulphur atom.[1] A new aspect of the study of the electrophilic activity of the triple bond in ethynyl ethers and sulphides involves the investigation of the addition of organometallic and organophosphorus reagents. The high regio- and stereoselectivities of the addition of organometallic reagents to ethynyl ethers and sulphides make it possible to obtain vinyl ethers and sulphides with a specified structure. Thus mixed organic copper-magnesium (lithium) compounds and Grignard reagents add to ethynyl ethers and sulphides with the mode of addition of the organic group characteristic of nucleophiles.[3,262–264] The hydrolysis of the intermediate and treatment with carbon dioxide or iodine lead to the formation of the *cis*-isomers of substituted vinyl ethers and sulphides:

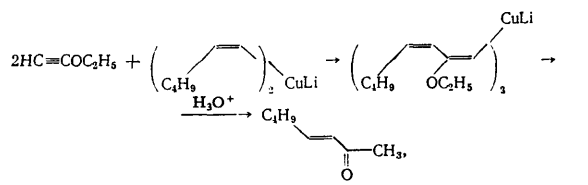
$$HC{\equiv}COC_2H_5 \xrightarrow{RCu.MgBr} [CH(Cu,\ MgBr){=}C(R)OC_2H_5] \xrightarrow[(CO_2,\ I_2)]{H_2O} \rightarrow XCH{=}C(R)OC_2H_5,$$

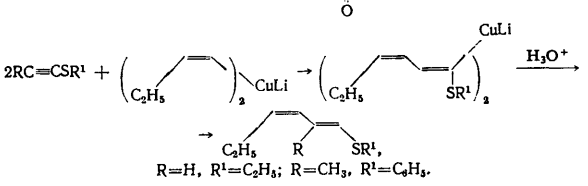
$$HC{\equiv}CSC_2H_5 \xrightarrow{RCU.MgBr} [RCH{=}C(Cu,\ MgBr)SC_2H_5] \xrightarrow[(CO_2,\ I_2)]{H_2O} \rightarrow RCH{=}C(X)SC_2H_5,$$

R = alkyl; X = H, COOH, I.

Phenylmagnesium bromide adds chemoselectively to 1-methylthiohexa-1,3-diyne in the presence of Ni^{2+} ions at the triple bond adjoining the sulphur atom with attachment of the phenyl group to the α-carbon atom and the predominant formation of (*E*)-ethynylvinyl sulphide.[265]

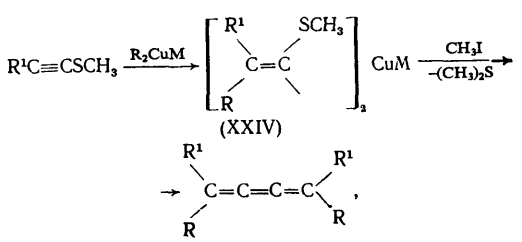
A vinylketone has been obtained by the reaction of an ethylenic lithium cuprate with ethoxyacetylene.[266] 1,3-Dienyl sulphides have been obtained from ethynyl sulphides under similar conditions:





R=H, $R^1=C_2H_5$; $R=CH_3$, $R^1=C_6H_5$.

The methylation of the intermediate (XXIV) by methyl iodide leads to the elimination of the methylthio-group and the formation of a vinylidene, which is converted into a cumulene hydrocarbon:[3,267]



R, R^1 = alkyl, M = MgHal, Li.

The copper-aluminium hydride complex adds to ethynyl sulphides regio- and stereo-selectively; (*Z*)-vinyl sulphides are formed after hydrolysis:[268]

$$RC{\equiv}CSR^1 \xrightarrow{\text{"CuH"}} [RCH{=}C(Cu)SR^1]^-Li^+ \xrightarrow{H_2O} RCH{=}CHSR^1,$$

R = alkyl, R^1 = alkyl, Ph; "CuH" = $LiCuHBr.Al(OCH_3)_3$.

In the absence of copper ions, the reaction with lithium trimethoxyhydroaluminate affords a mixture of regioisomers of (*E*)-vinyl sulphides.[269]

The 1,4-addition of alkylsilver to vinylethynyl sulphides leads to allenyl sulphides after hydrolysis:[270]

$$CH_2{=}CR^1C{\equiv}CSCH_3 \xrightarrow{RAg} RCH_2C(R^1){=}C{=}CHSCH_3,$$

R^1 = H, CH_3; R = alkyl.

Lithium alkyls add to ethynyl ethers with formation of allenyl and ethynyl ethers, whose ratio depends on the structure of the lithium alkyl, the ethynyl ether, and the solvent:[271]

$$R^2R^3C(OR^1)-C{\equiv}C-OR \xrightarrow{R^4Li} R^2R^3C{=}C{=}CR^4(OR) + R^2R^3C(OR^1)-C{\equiv}C-R^4,$$

R, R^1 = alkyl; R^2, R^3 = H, alkyl; R^4 = alkyl, Ph.

The chemoselective addition of lithium alkyls to the double bond in vinyl ethynyl sulphides is a convenient method of synthesis of allenyl sulphides.[272–274] The ambient nature of the intermediate in this reaction makes it possible to obtain alkylthioethynylcarbinols on oxidation of the intermediate by oxygen[275] or silicon-containing ethynyl sulphides on treatment with chlorotrimethylsilane.[276]

The acetylenic carbon atom–selenium bond in ethynyl selenides is readily cleaved on treatment with a lithium alkyl.[110] The reaction of phenyltelluroacetylene with butyllithium involves the simultaneous cleavage of the acetylenic carbon atom–tellurium bond and substitution at the acetylenic carbon atom.[68]

The synthetic possibilities of the reactions of organometallic compounds with vinylethynyl sulphides have been considered in a review.[277] On treatment with lithium alkyls of alkyl diacetylenic sulphides, the alkylthio-groups are substituted and diacetylenic hydrocarbons are formed.[233]

The reactions of vinylethynyl sulphides, selenides, and tellurides with lithium in liquid ammonia lead to the substitution of the alkyl group in the sulphides and of the alkylheteroatom group in the selenides and tellurides.[278] The alkyl group in the sulphides can be substituted by employing acetoxydiazomethane in the presence of copper salts.[3,279]

A method has been developed for the synthesis of tin- and lead-containing vinyl ethers and sulphides by the coupled hydrostannylation or hydroplumbylation of ethynyl ethers and sulphides.[280–284] The regioselectivities are different for ethers and sulphides:

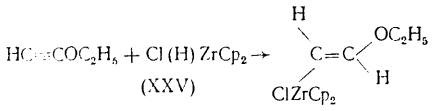
$$HC{\equiv}COR \xrightarrow{(C_2H_5)_3MNa} CH_2{=}C[M(C_2H_5)_3]OR,$$

$$HC{\equiv}CSR \xrightarrow{(C_2H_5)_3MNa} (C_2H_5)_3MCH{=}CHSR,$$

M = Sn, Pb; R = CH_3, C_2H_5.

In the stannylation reaction, tin-containing ethynyl ethers and sulphides are formed as side products. The metallation process predominates in the reaction of phenoxyacetylene with triethylgermyl-lithium.[203] The Schwartz reagent (XXV) adds regio- and

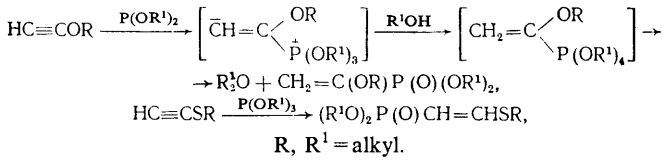
stereo-specifically to ethoxyacetylene with formation of an (*E*)-vinyl ether in which zirconium is readily substituted by electrophiles.[285,286]



(XXV)

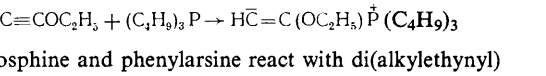
Cp = cyclopentadienyl.

Di- and tri-alkyl phosphites undergo the opposite type of addition to ethynyl ethers and sulphides:[287–294]

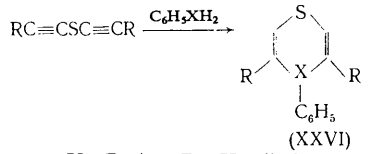


R, R^1 = alkyl.

According to the authors, the product of the addition of tributylphosphine to ethoxyacetylene has the structure of a dipolar ion:[295–298]



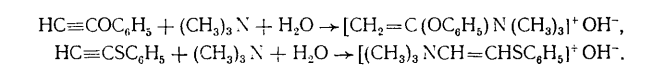
Phenylphosphine and phenylarsine react with di(alkylethynyl) sulphide in liquid ammonia in the presence of lithium amide to form the heterocyclic compounds (XXVI):[299]



(XXVI)

X = P, As; R = H, alkyl.

Tertiary amines readily add to terminal ethynyl ethers and sulphides in aqueous solution with the opposite mode of addition:[300]

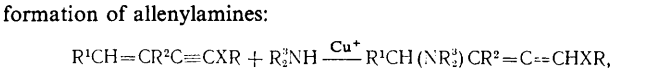


Internal phenoxy- and phenylthio-acetylenes do not react with triethylamine.

The addition of secondary amines to ethynyl sulphides leads to thioamides.[79,80,84] In the presence of an electron-accepting group at the triple bond in the ethynyl sulphide molecule, the usual mode of addition of amines changes and the amino-group is attached to the α-carbon atom of the triple bond.[118] Di(alkylthio)acetylenes and their selenium and tellurium analogues combine with diethylamine non-stereoselectively with formation of vinylamines.[301]

2-Methyloxazoline has been obtained as a result of the double addition of monoethanolamine to phenoxyacetylene.[224]

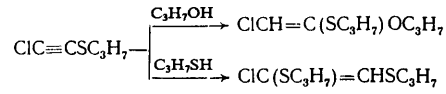
Secondary amines add to vinylethynyl sulphides,[302] selenides, and tellurides[303] in the presence of copper ions as the catalyst with formation of allenylamines:



X = S, Se, Te; R^1, R^2 = H, alkyl; R = alkyl; R^3 = alkyl, organyl.

Ethynyl ethers[39] and sulphides[118] with an electron-accepting group at the triple bond combine with phenol and methanol with a similar mode of addition. The mode of addition of allyl alcohols to phenoxyacetylene[304] is the same as that in the addition of ethanol to ethoxyacetylene.[1] Intramolecular cyclisation occurs in the reactions of acylthioacetylenes with alcohols.[305,306]

The different modes of addition of alcohols and mercaptans to 1-chloro-2-propylthioacetylene[307] are a consequence of the charge and orbital control of the reactions:



The addition of mercaptans to phenoxyacetylene[308] and ethynyl sulphides[9,88,309] takes place in conformity with the familiar rules.[1] Lithium methane-thiolate reacts with vinylethynyl sulphides chemoselectively via the triple bond with the attachment of the methylthio-group to the β-carbon atom and the formation of a (*Z*)-1,3-diene bis-sulphide:[310]

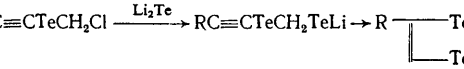


The attachment of the phenylthio-group to the α-carbon atom takes place in the addition of benzenethiol to ethynyl sulphides with electron-accepting substituents at the triple bond.[259]

The addition of sodium sulphide (selenide, telluride) to diethynyl sulphides leads to the formation of substituted 1,4-dithianes and their analogues:[5,311]

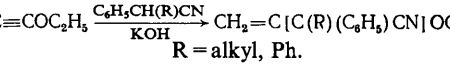
X = S, Se, Te; R = alkyl, isopropenyl.

Ethynyl tellurides react with lithium telluride, affording a substituted 1,3-ditellurole:[87]



R = H, alkyl, Ph.

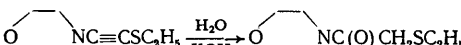
The rule governing the addition of nucleophiles holds in the reaction of a carbanion to ethoxyacetylene:[312]



R = alkyl, Ph.

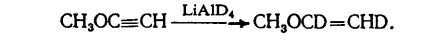
Ethynyl sulphides react non-regioselectively under similar conditions.

The mode of hydration of ethylthioethynylmorpholine in an alkaline medium is determined by the polarisation of the triple bond by the morpholino-group:[54]



Alkaline hydrolysis of 1-thiacyclooct-2-yne leads to the cleavage of the acetylenic carbon atom–sulphur bond.[107]

The reduction of methoxyacetylene with lithium tetradeuterio-aluminate constitutes a method of synthesis of deuteriated vinyl ethers:[313,314]



Ethynyl selenides can be hydrogenated by lithium tetrahydro-aluminate with formation of (*Z*)-ethynyl selenides.[110] The hydrogenation of vinylethynyl sulphides by lithium tetrahydro-aluminate in the presence of copper bromide leads to (*Z*)-1,3-dienyl sulphides, while in the absence of copper ions their (*E*)-isomers are formed.[315]

3. The radical addition reactions

Radical reagents add to ethynyl ethers and sulphides as a rule with the attachment of the radical to the β-carbon atom of the triple bond.[1] However, exceptions are known. Thus the reactions involving the photochemical addition of phosphorus tribromide to terminal ethynyl ethers[316] and sulphides[198] take place in different ways:

$$ROC{\equiv}CH + PBr_3 \xrightarrow{h\nu} ROC(PBr_2){=}CHBr,$$
$$RSC{\equiv}CH + PBr_3 \xrightarrow{h\nu} RSC(Br){=}CHPBr_2,$$
$$R = \text{alkyl}.$$

The free-radical addition of mercaptans to ethoxy- or phenoxyacetylene[308,317,318] and to substituted ethynyl sulphides[9,39,118] takes place in accordance with the familiar rule.

In the case of vinyl ethynyl sulphides, mercaptans undergo radical addition to the double bond:[319]

$$CH_2{=}CHC{\equiv}CSCH_3 + C_2H_5SH \rightarrow C_2H_5SCH_2CH_2C{\equiv}CSCH_3.$$

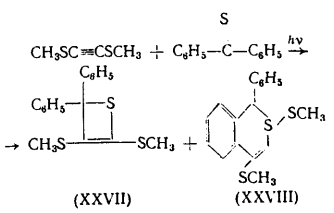
Under similar conditions, vinylethynyl selenide combines with ethanethiol via both multiple bonds with formation of a mixture of isomers.

Grignard reagents add chemoselectively and regioselectively to vinylethynyl sulphides at the double bond with formation, after hydrolysis, of a mixture of acetylenic (75%) and allenic isomers:[320,321]

$$CH_2{=}CHC{\equiv}CSR \xrightarrow{R^1MgHal} R^1CH_2CH_2C{\equiv}CSR + R^1CH_2CH{=}C{=}CHSR,$$
$$R,\ R^1 = \text{alkyl}.$$

Under similar conditions, 1-methylselenobut-3-en-1-yne forms an allenyl selenide in 38% yield. Vinylethynyl tellurides react with cleavage of the acetylenic carbon atom–tellurium bond.[322]

The mode of photochemical addition of ethynyl ethers[323,324] to ketones is of the usual type.[1] Thioketones add to di(methylthio)acetylene predominantly in accordance with the [2 + 2]cycloaddition mechanism with formation of compounds (XXVII). The [4 + 2]-cycloaddition product (XXVIII) is formed in 5–10% yield:[325–329]



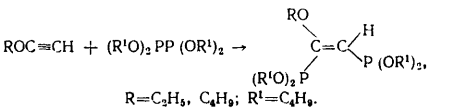
(XXVII) (XXVIII)

The reaction of 1,2-diones with ethynyl sulphides leads to the formation of a mixture of (*Z*)- and (*E*)-alkylthiobut-2-ene-1,4-diones.[3] Products having a similar structure have been obtained as a result of the [2 + 2]cycloaddition of phenanthrenequinone to internal ethynyl sulphides.[330]

The free-radical addition of trialkylgermanes and trialkyl- or triphenylstannanes to terminal ethynyl ethers[331] is similar to the already known reaction of trialkylstannanes.[1] The mode of addition of trialkylstannanes is retained in relation to silicon-, germanium-, and tin-containing ethynyl ethers.[6,212]

A substituted triazole adds to methoxyacetylene at the triple bond with the attachment of the triazole ring at the α-position relative to the methoxy-group.[332]

Tetraalkoxydiphosphines add stereospecifically to terminal ethynyl ethers:[333]



$R = C_2H_5,\ C_4H_9;\ R^1 = C_4H_9.$

The hydrogenation of ethoxyacetylene in the presence of a palladium catalyst has been investigated.[334] Vinylethynyl sulphides are slowly reduced at the palladium catalyst to the (*Z*)-1,3-dienyl sulphides.[335] The attempts to reduce ethynyl tellurides by various reductants led to the cleavage of the acetylenic carbon atom–tellurium bond.[69]

The energy of the interaction of singlet oxygen with dimethoxyacetylene has been calculated by the INDO method; a mechanism has been proposed for the oxidation reaction.[336]

The photochemical interaction of 1,4-dithiine and its homologues with di(ethylthio)acetylene leads to the formation of unstable coloured complexes as a result of [2 + 2]cycloaddition.[337]

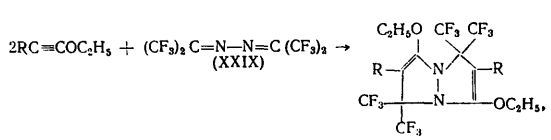
For the electrochemical reduction and oxidation of ethynyl sulphides, selenides, and tellurides, see Tomilov et al.[338]

4. Cycloaddition

The cycloaddition reactions of ethynyl ethers and sulphides with diazomethane, organyl azides, 1,3-dipolar reagents, ketens, cyclic ketones, and 1,3-dienes have been developed further.[1] Diazomethane adds to methoxyacetylene,[339] 4-bromo-1-methoxy-4-methyl-3-oxopent-1-yne,[220] and silicon-, germanium-, and tin-substituted ethynyl ethers[340] with formation of the corresponding 4-alkoxypyrazoles, similarly to the familiar reaction of ethoxyacetylene.[1] The reaction of dimethyldiazomethane with terminal ethynyl sulphides[341] leads to the predominant formation of the product of the opposite mode of addition, similarly to the familiar reaction of ethylthioacetylene.[1]

The reaction of organyl azides with ethoxyacetylene[1] has been used to obtain a series of substituted 1,2,3-triazoles,[342–344] one of which is a potential antibiotic.[345]

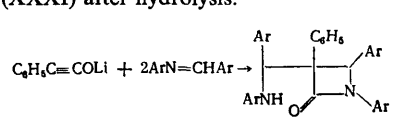
Hexafluoroacetone azene (XXIX) reacts with two molecules of ethynyl ether to form a mixture of compound (XXX) and its regioisomers:[346–348]



(XXIX) (XXX)

R=H, CH_3.

Aromatic imines add to lithium phenylethynoxide with formation of compound (XXXI) after hydrolysis:[349]

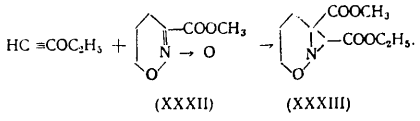


(XXXI)

The 1,3-dipolar cycloaddition of nitrile oxides to ethoxyacetylene has been used in the synthesis of isoxazole-containing *C*-nucleosides[350] and other isoxazole derivatives.[351]

The perturbation energy of the methoxyacetylene MO in the reaction with 1,3-dipoles has been calculated by quantum-chemical methods.[352,353]

Oxazine *N*-oxide (XXXII) reacts with ethoxyacetylene to form the aziridine derivative (XXXIII):[354]

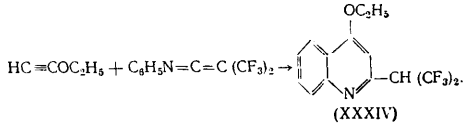


(XXXII) (XXXIII)

The nitro-derivative of the *N*-oxide reacts with elimination of the nitro-group and the formation of a substituted oxazine.[355,356]

The [2 + 2]cycloaddition of dimethylketen,[357,358] dichloroketen,[359] ring-containing ketens,[360,361] and vinylketen[362] to ethoxyacetylene and of dichloroketen to silicon- and germanium-containing ethynyl ethers[363] leads to the formation of the corresponding cyclobutenones, similarly to the familiar reactions.[1] The reaction of bis(trifluoromethyl)keten with silicon- and germanium-containing ethynyl ethers affords products having a linear structure in addition to the substituted cyclobutenone.[363] Aromatic ketens react as a rule with ethoxyacetylene via the [2 + 2]- and [2 + 2 + 2]cycloaddition mechanisms.[362,364] The mode of reaction of diphenylketen with ethoxyacetylene has been calculated by the CNDO/2 method.[365] Diphenyl keten reacts with organylthioalkynes via the [2 + 2]cycloaddition mechanism.[92]

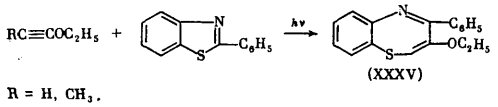
The [2 + 4]cycloaddition of *N*-phenylbis(trifluoromethyl)keten imine to ethoxyacetylene leads to the formation of the ethoxyquinoline (XXXIV):[366]



(XXXIV)

Isocyanates react with organylthioalkynylamines[92] and thioisocyanates react with 1-ethoxyprop-1-yne[367] in accordance with the [2 + 4]cycloaddition mechanism.

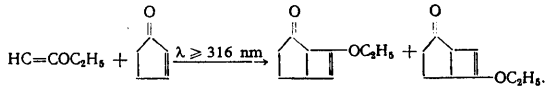
The photocyclisation reaction of 2-phenylbenzothiazole with ethynyl ethers, accompanied by linear expansion, leads to the formation of substituted 1,5-benzothiazepines (XXXV):[368,369]



(XXXV)

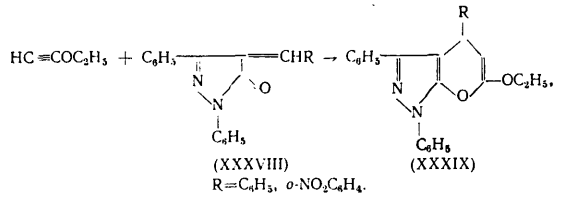
R = H, CH_3.

The photochemical [2 + 2]cycloaddition of 2-cyclopent-1-enone to ethoxyacetylene proceeds with a low regioselectivity—compounds (XXXVI) and (XXXVII) are formed:[370,371]



The photocycloaddition of 5,8,9,10-tetrahydro-*p*-naphthoquinone to ethoxyacetylene leads to the formation of 4-ethoxy-2,7-dioxotricyclo-[6.4.0.0^{3,6}]dodeca-4,10-diene.[372]

Cyclopentadiene enters into the Diels–Alder reaction with 1,3-dimethoxy-3-oxoprop-1-yne and 3-methoxy-1-phenylthio-3-oxoprop-1-yne.[373] Compounds (XXXIX) have been obtained by the [2 + 4]cycloaddition of arylidenepyrazolones (XXXVIII) to ethoxyethylene:[374]

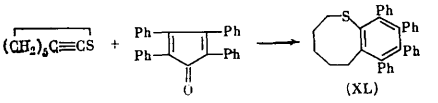


(XXXVIII) (XXXIX)

R = C_6H_5, *o*-$NO_2C_6H_4$.

Substituted 3-methyleneoxindole reacts with ethoxyacetylene similarly.[375]

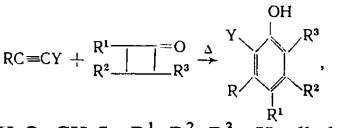
A tetrasubstituted cyclopentadienone reacts quantitatively with 1-thiacyclooct-2-yne, forming compound (XL):[107]



(XL)

The perturbation energy of the MO of 2-pyridone and ethoxyacetylene in the [2 + 4]cycloaddition reaction has been calculated by the CNDO/2 method.[376]

Substituted phenols have been obtained by heating ethynyl ethers and sulphides with cyclobutenone:[377]



R = alkyl, Y = CH_3O, CH_3S; R^1, R^2, R^3 = H, alkyl, C_2H_5O, Cl.

5. Substitution reactions

It was established previously that alkylheteroatom groups are substituted in the reactions of internal ethynyl ethers and sulphides with organolithium compounds.[1] The effect of organyl halides on element-containing ethynyl sulphides with heteroatoms at the sulphur atom has been studied. Thus treatment of ethoxy(trimethylsilyl)-acetylene with an excess of bromotrimethylsilane afforded bis-(trimethylsilyl)keten.[2]

The reaction of lithium dialkylamides with alkoxy(silyl)- and alkoxy(germyl)-acetylenes leads to the formation of silyl- and germyl-alkynylamines:[378]

$$R^1_3MC{\equiv}COR \xrightarrow{R_2NLi} R^1_3MC{\equiv}CNR_2,$$

M = Si, Ge; R, R^1 = alkyl.

Ethoxy(trimethylstannyl)acetylene reacts with lithium diethylamide with cleavage of the tin–carbon atom bond. Transmetallation of ethoxy(trimethylstannyl)acetylene yielded a germanium-containing ethynyl ether.[6]

Alkoxyethynyl ketones have been synthesised by treating tin-containing ethynyl ethers with carboxylic acid chlorides:[220,379]

$$(CH_3)_3SnC{\equiv}COR \xrightarrow{R^1COCl} R^1COC{\equiv}COR,$$

R = alkyl, R^1 = organyl.

Tin-containing alkynylamines have been obtained in 40% yield by the reaction of ethoxy(trimethylsilyl)acetylene with diethyl-(trimethylstannyl)amine:

$$(CH_3)_3SiC{\equiv}COC_2H_5 \xrightarrow{(CH_3)_3SnN(C_2H_5)_2} (CH_3)_3SnC{\equiv}CN(C_2H_5)_2.$$

Diethylamino(trimethylsilyl)acetylene is formed as an intermediate.

The methylseleno-group is readily substituted by the triethylstannyl group in reactions of di(methylseleno)acetylene with triethylstannylsodium in liquid ammonia.[380]

Trialkylstannylthioacetylenes have been obtained by substituting the acetyl group in acetylthioacetylenes by the trialkylstannyl group:[381,382]

$$RC{\equiv}CSCOCH_3 \xrightarrow{R_3SnOR} RC{\equiv}CSSnR_3,$$
$$R = \text{alkyl}.$$

The "transmetallation" reactions of compounds (XLI) have been described:[94,381,382]

$$RC{\equiv}CSMR_3 \xrightarrow{R^1_3M^1X} RC{\equiv}CSM^1R^1_3,$$
(XLI)
$$M{=}Sn,\ M^1{=}Si,\ Ge;\ M{=}Si,\ M^1{=}Ge,\ Sn,\ Pb.$$

The trialkylsilyl group at the sulphur atom is readily split off on treatment of compound (XLII) with methanol with formation of compound (XLIII):[94]

$$(CH_3)_3SiC{\equiv}CSSi(CH_3)_3 \xrightarrow{CH_3OH} [(CH_3)_3SiC{\equiv}CSH] \rightarrow$$
(XLII)
$$\rightarrow [(CH_3)_3SiCH{=}C{=}S] \xrightarrow{CH_3OH} (CH_3)_3SiCH_2C(S)OCH_3.$$
(XLIII)

The cyano-group in ethynyl thiocyanates is substituted on treatment with lithium acetylide[5,311] or lithium dialkylamide:[90]

$$RC{\equiv}CSCN \xrightarrow{LiC{\equiv}CR^1} RC{\equiv}CSC{\equiv}CR^1$$
$$RC{\equiv}CSCN \xrightarrow{R_2NLi} RC{\equiv}CSNR_2$$
$$R = \text{alkyl},\ R^1 = R_3Si.$$

Ethynyl disulphides react with secondary amines at 0 °C with cleavage of the sulphur–sulphur bond and the addition of an amine molecule to the thioketen formed.[89]

Ethynyl sulphides are oxidised by an equimolar amount of H_2O_2 in acetic anhydride with formation of ethynyl sulphoxides:[383,384]

$$HC{\equiv}CSR \xrightarrow{[O]} HC{\equiv}CS(O)R,$$
$$R = \text{alkyl}.$$

Terminal ethynyl sulphones have been obtained by oxidising ethynyl sulphides with acetyl hydroperoxide[385] or with hydrogen peroxide.[386]

Phenylethynyl selenides are oxidised by *m*-chloroperbenzoic acid with cleavage of the acetylenic carbon atom–selenium bond:[387]

$$RC{\equiv}CSeR^1 \xrightarrow{m\text{-}ClC_6H_4COOOH} RC{\equiv}CC{\equiv}CR,$$
R-aryl, cyclohexenyl; R^1 = alkyl, aryl.

In the presence of water, only terminal acetylenic hydrocarbons are formed.[388]

In contrast to ethynyl sulphides and selenides, ethynyl tellurides give rise to telluronium compounds in the reaction with ethyl iodide.[231,389,390] The ammonium salt is formed in the reaction of ethylthiomorpholinoacetylene with methyl iodide.[54]

6. Complex formation

It was shown previously that methoxyacetylene readily forms a complex with iron carbonyl.[1]

The carbene complex of tungsten pentacarbonyl (XLIV) adds to the triple bond of ethoxyacetylene with formation of the unstable complex (XLV), which isomerises to the complex (XLVI):[391]

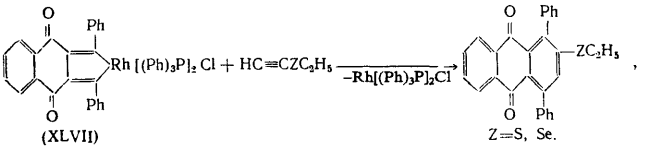
$$HC{\equiv}COC_2H_5 + (CO)_5W{=}CHC_6H_5 \rightarrow \left[(CO)_5W{-}\underset{\displaystyle C_2H_5O{-}C{=}CH}{\overset{\displaystyle C_6H_5}{\overset{|}{C}H}}\right] \rightarrow$$
(XLIV) (XLV)
$$\rightarrow (CO)_5W{=}C(OC_2H_5)CH{=}CHC_6H_5.$$
(XLVI)

Ruthenium carbonyl hydrides react with ethoxyacetylene to form the allyltriruthenium cluster.[392] Aromatic compounds have been obtained by the reaction of cyclobutadiene-tricarbonyliron with ethoxyacetylene.[393] The reaction of internal ethynyl ethers with carbene pentacarbonylchromium also leads to the formation of aromatic compounds.[394,395]

Dimethoxyacetylene forms complexes with iron nonacarbonyl and cobalt octacarbonyl at –60 °C:[26]

$$CH_3OC{\equiv}COCH_3 \xrightarrow{Fe_2(CO)_9} (CH_3OC{\equiv}COCH_3)_2Fe(CO)_6.$$

Substituted anthraquinones have been obtained by the reaction of the rhodium complex (XLVII) with ethylthio- and ethylseleno-acetylenes:[396]



Di(methylthio)acetylene forms complexes with cyclopentadienylmolybdenum and cyclopentadienyltungsten carbonyls and iron, cobalt, and ruthenium carbonyls.[397,398] In the complex with tungsten carbonyl, the di(methylthio)acetylene ligand is substituted in the reaction with bis(dimethylphosphino)ethane.[399]

In the reaction with 1-t-butylthioprop-1-yne, the dimeric tungsten t-butoxide gives rise to an unstable tungsten complex:[400]

$$CH_3C{\equiv}CSR \xrightarrow{W_2(OR)_6} (RO)_3W{\equiv}CSR,$$
$$R = t\text{-}C_4H_9.$$

Aryl ethynyl sulphides and their analogues $p\text{-}XC_6H_4EC{\equiv}CC_6H_4Y\text{-}p$ (E = S, Se, Te; X = H, CH_3OCH_3, F, Cl, Br; Y = H, Cl) form charge-transfer complexes with tetracyanoethylene, the tellurides being the strongest electron donors in this series.[401] The pentafluorophenyl derivatives of the sulphides do not form charge-transfer complexes with tetracyanoethylene as a consequence of the reduced electron-donating capacity of the $-C{\equiv}C-S-$ fragment.[65]

7. Rearrangements and isomerisation

It was established previously that allenyl ethynyl sulphides undergo the thio-Claisen rearrangement in the presence of secondary amines.[1] The study of this rearrangement was continued in the presence of secondary amines[83,93,402,403] and lithium amides[404] and on heating.[97] Allenyl ethynyl selenides undergo the same rearrangement.[98]

Methoxyethynylphosphine undergoes an unusual rearrangement in the course of its synthesis with formation of compound (XLVIII):[113]

$$R_2PC{\equiv}COCH_3 \rightarrow R_2(CH_3)P{=}C{=}C{=}O,$$
(XLVIII)
$$R = \text{alkyl, aryl}.$$

The sigmatropic rearrangement of ethynyl sulphides takes place in the presence of sodium amide and bromobenzene in liquid ammonia:[405]

$$RCH_2C{\equiv}CSCH_2R^1 \xrightarrow[NaNH_2]{C_6H_5Br} C_6H_5SCHR^1CHRC{\equiv}CH,$$
$$R,\ R^1{=}H,\ CH_3.$$

Internal ethynyl ethers and sulphides are known to isomerise readily to allenyl ethers and sulphides in the presence of bases.[1] 3-Methoxy-1-methylthioprop-1-yne isomerises to the methylthioallenyl ether in the presence of lithium diisopropylamide.[3] Allenyl sulphides have been obtained by the isomerisation of other ethynyl sulphides under similar conditions.[406,407]

8. Thermolysis and polymerisation

The thermal decomposition of ethynyl ethers and sulphides, leading to the formation of ketens and thioketens, has been examined in other reviews.[1,6] Pyrolysis of methoxyacetylene at 600 °C for 10 min leads to the formation of formaldehyde, acetylene, ethylene, and ethane.[408] The gas-phase pyrolysis of di(phenylthio)-acetylene at 560 °C afforded mainly diphenyl sulphide, thiophenol, and acetylene.[409]

The polymerisation of ethynyl ethers has been examined in a review.[1] The study of the polymerisation process was later extended to ethynyl sulphides.[410,411]

In the presence of boron trifluoride, diethylamino(phenylthio)-acetylene dimerises:[412]

$$2\,C_6H_5SC{\equiv}CN(C_2H_5)_2 \xrightarrow[THF]{BF_3} (C_2H_5)_2N{-}C{=}C{-}SC_6H_5$$
$$\qquad\qquad\qquad

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