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REACTIONS OF TRIADS S_8–KOH–DMSO, Se_8–KOH–DMSO, Te–KOH–HMPA WITH ACETYLENES

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Abstract—A new general approach to anionic transformations of acetylenes using superbasic media has been developed. It allows series of new reactions which are not undergone by acetylene under conventional conditions. The triads S_8-KOH-dimethylsulfoxide (DMSO), Se_8-KOH-DMSO, Te-KOH-hexamethyl-phosphorictriamide (HPMA) are proposed as new effective reagents for the preparation of unsaturated compounds of sulfur, selenium and tellurium. A series of reactions of acetylene with sulfur, selenium and tellurium proceeding in DMSO or HMPA in the presence of alkali and water at 80–120° leading to divinyl sulfide, divinyl selenide and divinyl teluride in 25–80% yields have been found. Thiophen, di-1-(1,3-butadienyl) sulfide, 1-vinyl-2-thiabicyclo[3.2.0]hept-3-ene, and dihydrothiophen have been obtained by the reaction of vinylacetylene with sulfur. The reaction of vinylacetylene with selenium affords selenophen, di-1-(1,3-butadienyl) selenide, 1-vinyl-2-selenabicyclo[3.2.0]hept-3-ene, methyl (1-(1,3-butadienyl) sulfide, and methylthiomethyl 1-(1,3-butadienyl) selenide, vinyl 1-(1,3-butadienyl) sulfide, and methylthiomethyl 1-(1,3-butadienyl) selenide (the latter two with DMSO participation). The reaction of vinylacetylene with tellurium gives mainly di-1-(1,3-butadienyl) telluride. A series of reactions between DMSO and selenium leading to dimethyl sulfide, dimethyl sulfoselenide, and methylthiomethyl selenide have been observed.

For the last decade we have been exploring systematically a new approach to bring about anionic transformations of acetylenes using superbasic systems.[1] It affords a variety of unusual reactions.[2–6] Among them there are interactions of acetylene with sulfur[3,4] and other chalcogens[3,5,6] in systems consisting of dimethyl sulfoxide (DMSO) or hexamethylphosphorictriamide (HMPA) and alkali metal hydroxides.

In such conditions sulfur is readily transformed into divinyl sulfide 1 in about 80% yield based on two sulfur equivalents giving one equivalent of sulfide ions.[7] The preferable temperature interval lies between 80° and 120°. Small amounts of water are necessary as a proton transfer agent.[4] It should be emphasized that the solvent plays a decisive role in this synthesis. Suitable results are attained only in such an aprotic dipolar solvent as DMSO and HMPA which are stable enough when heated in the presence of strong bases. In other solvents, there is no reaction at all or there is a very slow and ineffective one. For instance at 110–120° in dioxan the yield of sulfide 1 never exceeds 7%, while the yield in HMPA is 76%, and that in DMSO is 80%.

1, 80%

Experiments show that at a higher temperature (130–140°) thiosulfate formed in the above reaction, reacts with acetylene affording sulfide 1 in about 40% yield. In the case of substituted acetylenes such as phenylacetylene, the corresponding substituted divinyl sulfides are formed.

$$K_2S_2O_3 + H_2O + HC{\equiv}CH \xrightarrow[130\text{–}140^\circ]{DMSO} \underset{40\%}{1} + K_2SO_4$$

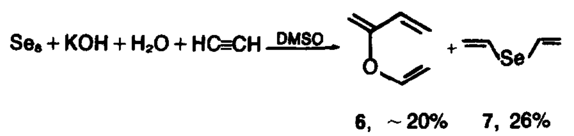
$$K_2S_2O_3 + H_2O + HC{\equiv}CPh \xrightarrow[165\text{–}175^\circ]{DMSO} (PhCH{=}CH)_2S + K_2SO_4$$

$$\sim 40\%$$

Reactions are of a rather general character and, as was already shown,[3] applicable to not only acetylene itself but to substituted acetylenes as well. However, in the case of vinylacetylene (Scheme 1), when the latter is reacting with sulfur in the KOH–DMSO system, some other reactions have been observed.[8] Besides di(1,3-butadienyl) sulfide 2, 2,5-dihydrothiophen 3, 1-vinyl-2-thiabicyclo[3.2.0]hept-3-ene 4, and thiophen 5 were isolated. The former two heterocycles could be expected to be formed knowing their easy formation from sulfide ions and vinyl acetylene under the same conditions[9] (Scheme 2).

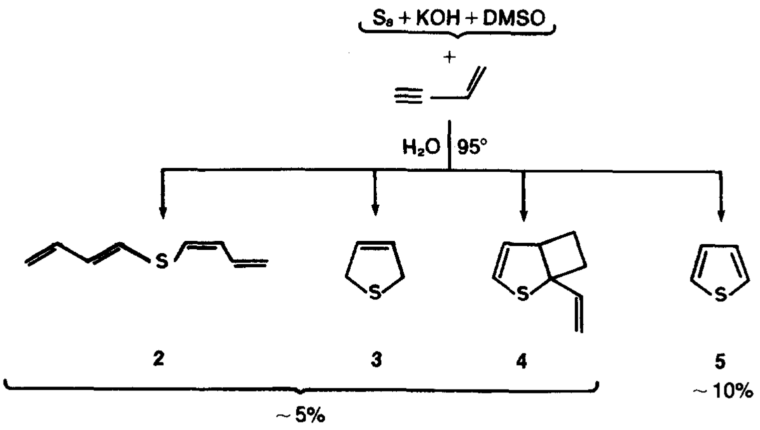
The above bridgehead thiabicycloheptene 4 is believed to form through the cyclization of the intermediate dibutadienyl sulfide carbanion (Scheme 3), the latter resulting from the addition of butadienthiolate anion to vinylacetylene at position 3. The ion pair cyclization can be facilitated by a template effect of potassium cation, providing both the vicinity and polarization of the systems.

When the selenium triad (Se-KOH-DMSO) interacts with acetylene, 2-vinyloxy-1,3-butadiene 6 is formed along with expected divinyl selenide 7, the latter yield (26%) being in agreement with the reaction scheme that three equivalents of selenium give two equivalents of 7.[5]

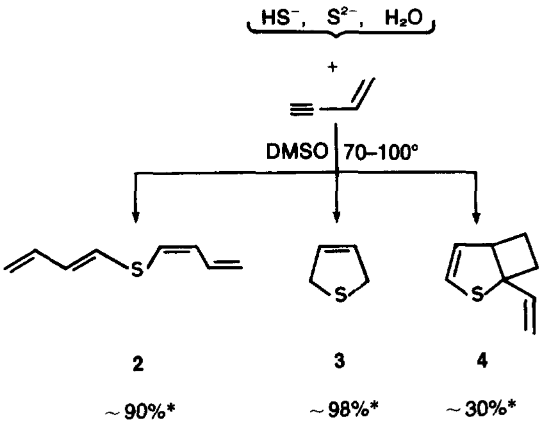


6, ~20%   7, 26%

Vinyloxylbutadiene 6 results from the hydration-trimerization processes of acetylene.[10] This reaction proceeds well in the absence of selenium in only the super-

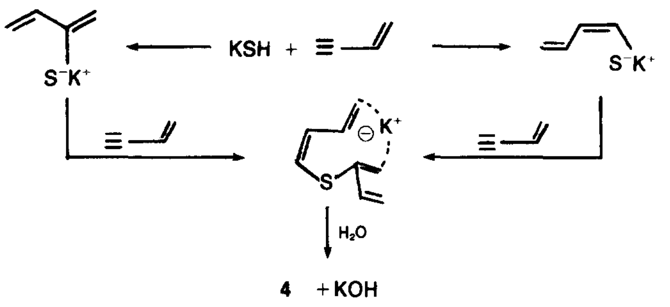


Scheme 1.



*depending on conditions[8]

Scheme 2.



Scheme 3.

basic KOH-DMSO system. As our investigations show, under specific conditions the yield of diene 6 can be as high as 80% (based on acetylene consumed).[11]

It seemed possible that sodium selenide, like sodium sulfide,[12] would react with acetylene to afford divinyl selenide. Contrary to these expectations, however, this

$$Na_2S + HC\equiv CH \xrightarrow[90^\circ]{H_2O,\ DMSO} 1 \quad 90\%$$

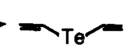
$$Na_2Se + HC\equiv CH \not\xrightarrow{H_2O,\ DMSO} 7$$

did not happen, only traces of divinyl selenide were found in the reaction mixture. Thus, though divinyl sulfide is preferably formed through the sulfide ion,[12] the divinyl selenide formation goes in another way.

As is known,[13] selenides are oxidized even by air in an alkali medium. Apparently, in our conditions, a rapid oxidation of selenide ions by DMSO is likely to occur.

The triad Te-KOH-DMSO also interacts with acetylene to give divinyl telluride 8. The temperature range of the reaction is 110–120°. We have found conditions affording divinyl telluride in a yield as high as 54%.[6] In this case, HMPA happened to be more effective than DMSO, in which the yield of divinyl telluride is not higher than 30%.

$$Te + KOH + H_2O + HC\equiv CH \xrightarrow[110\text{–}120^\circ]{HMPA}$$

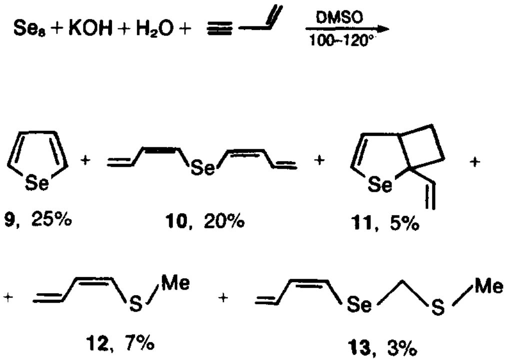


8, 54%

A direct synthesis of divinyl telluride from tellurium and acetylene opens up a new route to unsaturated tellurium compounds.

In superbasic systems (KOH-DMSO and KOH-HMPA), vinyl acetylene reacts with selenium at 100–120° to form selenophen 9, di-1-(1,3-butadienyl) selenide 10, and 1-vinyl-2-selena-bicyclo[3.2.0]hept-3-ene 11.[14] From the reaction mixture, methyl 1-(1,3-butadienyl) sulfide 12 and methylthiomethyl 1-(1,3-butadienyl) selenide 13 were also isolated, indicating DMSO participation in the reaction.[15]

Unlike the reaction of vinylacetylene with sulfur in which 2,5-dihydrothiophen is formed, no 2,5-dihy-



9, 25% 10, 20% 11, 5% 12, 7% 13, 3%

droselenophen was found in the reaction mixture. We could expect such a result, since the intermediate 1-(1,3-butadienyl) selenide anion should be more easily oxidized than its sulfur analogue.

In the superbasic system, tellurium also reacts with vinylacetylene at 100° to form a multi-component mixture containing more than 50% of di-1-(1,3-butadienyl) telluride **14**, the yield of which is about 3% (based on tellurium).[16]

14, 3%

The isomer ratio (Table 1) of di(1,3-butadienyl-1)chalcogenides **2**, **10**, **14** obtained varies depending on the reaction temperature and isolation procedure. In Table 1, the data for the samples prepared at 90–100° are presented. The trend to retain a cis-configuration on going from sulfur to tellurium is remarkable.[16]

The structure of all the compounds synthesized is reliably determined by a variety of spectral methods (IR, NMR,[16] and mass spectroscopy[17]). NMR spectra are especially informative in this respect. Figure 1 shows the ^1H NMR spectrum of 1-vinyl-2-selenabicyclo[3.2.0]hept-3-ene taken at 360 MHz. At such a frequency the spectrum can be easily analyzed by first order rules.

The only exception are the protons in position 7. Degeneracy due to a coincidence of their chemical shifts has been found in the double resonance spectrum under irradiation of these protons by second radiofrequency field.

As it has been noted above, there are some cases when DMSO itself takes part in the reactions. These processes are especially prominent in the selenium triad (Se-KOH-DMSO). After heating in this system the following products were formed: dimethyl sulfide, dimethyl disulfide, dimethyl diselenide, dimethyl sulfoselenide **15** and methylthiomethyl methyl selenide **16**.[15] These reactions display a higher reactivity of DMSO in the presence of selenium. In analogous conditions, but without

Table 1. Isomer ratios of $(CH_2=CH-CH=CH)_2E$* after ^1H NMR spectra

E	Configuration		Ratio, %
	cis,	cis	15
S	cis,	trans	70
	trans,	trans	15
	cis,	cis	60
Se	cis,	trans	33
	trans,	trans	7
	cis,	cis	90
Te	cis,	trans	6
	trans,	trans	4

*All compounds were obtained at 90–100°.

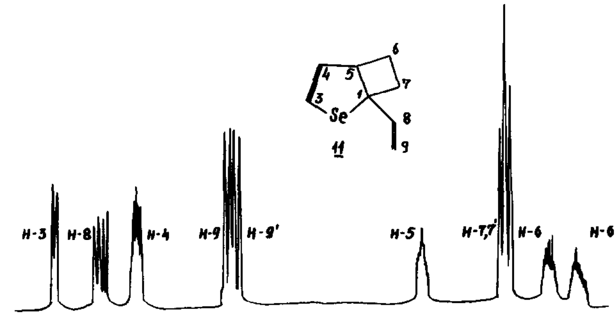
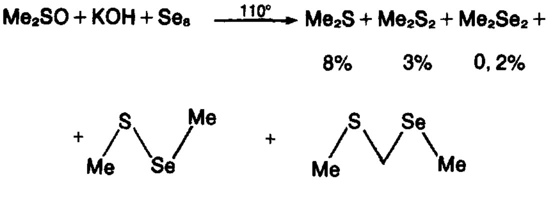


Fig. 1. ^1H NMR spectrum of 1-vinyl-2-selenabicyclo[3.2.0]-hept-3-ene (11) at 360 MHz.



15, 0,5% **16**, 0,1%

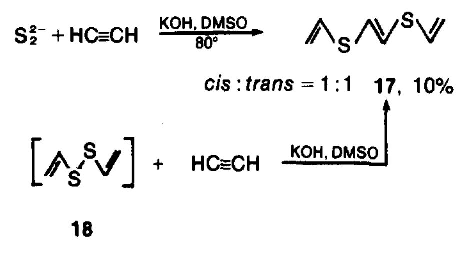
selenium, DMSO is stable. Selenium is known to play a catalytic role in a number of chemical and biochemical processes.[18] Obviously, in the reaction with DMSO, selenium behaves not only as a reagent but as a catalyst as well.

All the reactions considered occur in only superbasic systems of the KOH–DMSO type. The latter can be successfully substituted by HMPA in only some limited cases. The superbasicity of such systems is partly related to the ion pair separation by a strong specific solvation of the cation, on one hand, and formation of a highly basic and poorly solvated dimsylate ion, on the other hand.

It is known that in such systems the basicity estimated[19] from the acidity function, increases by many powers of ten and the free energy of anions rises sharply.[20] These desolvated anions become supernucleophiles capable to incorporate very smoothly into the triple bond. Since in such media the proton activity is lower, the role of the counter-ion in the transition state may belong to the cation of the alkali metal. The *ab initio* calculation performed recently by Eisenstein *et al.*,[21] has shown such a transition state to be more preferable, i.e. the alkali metal cation makes the nucleophile addition essentially easier than the proton does.

In the triads used, the initial anions are not monosulfides, selenides or tellurides but the relevant polychalocogen ones (for instance, polysulfide ions) having a higher nucleophilicy.

Stripping off the element atom, the initial adducts of such anions to acetylene, can be transformed into more stable divinyl derivatives with a single atom of the element. In fact, in the KOH–DMSO system at 110–120°, alkali metal polysulfides react with acetylene very smoothly to form divinyl sulfide in 70–90% yield (one equivalent of divinyl sulfide is formed from one polysulfide equivalent). Under milder conditions, sodium disulfide and acetylene afford, along with divinyl sulfide, 1,2-di(vinylthio)ethene **17** in 10% yield.[22] Its precursor seems to be divinyl disulfide **18** which adds to acetylene.



17, 10%

18

We have previously shown that such a reaction of acetylene with organic disulfides proceeds readily in the superbasic system consisting of DMSO and potassium t-butoxide.[23]

The reactions of triads in question with acetylene are complicated multistep processes, both nucleophilic and redox. The latter can be accelerated by the KOH–DMSO system, since the dimsylate anion is known to facilitate one-electron transfer as for reduction of ketones to the corresponding radical anions.[24]

Thus, one may see that a set of new monomers, chemicals and synthons are now becoming available owing to the above reactions of sulfur, selenium and tellurium with acetylene and its substitutes in superbasic media. Below are given only some illustrations (Scheme 4) concerning divinyl sulfide.

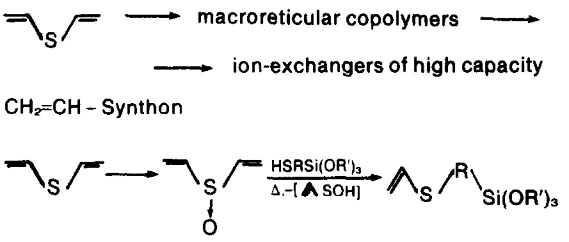
(a) Divinyl sulfide as a cross-linking agent affords macroreticular polymers. Ion-exchangers made of them possess an almost theoretical capacity with the ion exchange rate nearly as high as that of homogeneous reactions.

Sufilde **1** can be useful as a vinyl synthon. Various types of protogenic compounds readily undergo the base-catalysed addition to divinyl sulfoxide[25] which in turn is easily obtained from divinyl sulfide. On pyrolysis, the adducts eliminate vinylsulfenic acid to recover the vinylated addend.

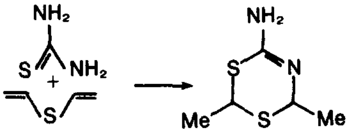
(b) Divinyl sulfide can also be used as a "building block" in the synthesis of new heterocyclic compounds. Scheme 4 shows the cycloaddition of thiourea to give 2,6-dihydro-2,6-dimethyl-4-amino-1,3,5-dithiazine.[26]

The results imply that the reactions of sulfur and other chalcogens with acetylene and its homologues in superbasic systems can provide useful starting materials for new reactions.

(a) Cross-linking agent



(b) "Building block" for heterocyclic syntheses



Scheme 4.

EXPERIMENTAL

^1H NMR spectra were measured on Varian XL-100, Bruker WH-270, Bruker WH-360 instruments. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer operating in Fourier mode. The NMR chemical shifts, δ, were in ppm and coupling constants, J, in Hz. Following abbreviations were used: doublet of singlets (ds), doublet of doublets (dd), quartet (g), multiplet (m). Mass spectra were taken on an MX-1303 instrument operating at 50 eV. IR spectra were obtained with UR-10 and UR-20 instruments in films in the 400–3600 cm^{-1}. Following abbreviations were used: strong (s), middle (m), weak (w), shoulder (sh). The glc analysis of the reaction mixtures was carried out on a LHM-72 instrument, with a Katharometer as a detector; column: 1 m × 4 mm with 15% Silicon DC-550 on Chromaton N-AW-DMCS or with 15% Carbowax 20 M on Chezasorb AW. Preparative chromatography (P GLC) was run using a PAHV-07 instrument, with a catharometer as a detector; column: 2 m × 40 mm packed as analytical one.

Reaction of acetylene with sulfur

(a) Powdered sulfur (6.4 g), KOH (22.4 g), H_2O (3.6 ml) in DMSO

(100 ml) were heated in 1 l rotating steel autoclave at 110–120° for 3 hr under acetylene pressure (initial—12 atm, residual—5 atm, 25 l of C_2H_2 in total). The reaction mixture was diluted with water and extracted with Et_2O. The extracts were washed with water, dried over K_2CO_3; the ether was evaporated. After distillation residue gave 6.9 g (80.2%) of divinyl sulfide **1**. B.p.$_{720}$ 84°, d_4^{20} 0.9098, n_D^{20} 1.5045, $M^{+\cdot}$ 86 (lit.,[27] b.p.$_{760}$ 84–86°, n_D^{20} 1.5060). The ^1H NMR spectrum (in CCl_4 with TMS as internal standard): 5.26 (=CH_2, dd, chemical shifts of both protons coincide), 6.39 (=CH, q, J_{cis} = 9.8, J_{trans} = 16.7). Dipole moment 1.20 D.

(b) Powdered sulfur (6.4 g), KOH (22.4 g), H_2O (7.2 ml) in HMPA (100 ml) were heated in a 1 l steel rotating autoclave at 110–120° for 3 hr under the acetylene pressure (initial—10 atm, residual—2 atm, 20 l of C_2H_2 in total). After the above work up, 6.5 g (75.6%) of **1** was isolated.

(c) When dioxan instead of DMSO of HMPA was used in the conditions of run (b) (initial pressure of C_2H_2—11 atm, residual—4 atm, 23 l of C_2H_2 in total), only 0.6 g (7%) of **1** was isolated.

Reaction of vinylacetylene with S–KOH–DMSO triad. Vinylacetylene (13 g) was bubbled through a flask equipped with a condenser and a stirrer, which contained sulfur (9.7 g), KOH (9.5 g), H_2O (20.4 g) in DMSO (100 ml). The reaction mixture was heated at 95° for 7 hr, allowed to cool to room temperature, diluted with water (50 ml) and extracted with Et_2O. The extracts were washed thrice with water and dried over $CaCl_2$; the ether was evaporated. Vacuum distillation of the residue followed by glc analysis using authentic samples gave 1.63 g (3.9%) of **2**, 0.2 g (0.7%) of **3**, 0.5 g (1.2%) of **4**, and 2.5 g (9.8%) of **5**. Yields were calculated based on the sulfur need.

Di-1-(1,3-butadienyl) sulfide (**2**). A mixture of $Na_2S{\cdot}9H_2O$ (57.6 g), KOH (1.7 g), vinylacetylene (25 g), and DMSO (100 ml) was heated (90–110°) in a rotating autoclave for 4 hr, then poured into water, and extracted with Et_2O. The extracts were washed with water and the solvent was removed. Vacuum distillation of the residue gave 20.1 g (90.5%) of **2**, b.p.$_6$ 75°, n_D^{20} 1.6053, $M^{+\cdot}$ 138. IR spectrum was discussed in Ref. 8.

From the reaction mixture was also isolated 0.9 g (4.1%) of **4**, b.p.$_{20}$ 85°, n_D^{20} 1.5415, $M^{+\cdot}$ 138.

2,5-Dihydrothiophen (**3**). Vinylacetylene (13 g) was bubbled through a vigorously stirred mixture consisting of NaSH (14.5 g), H_2O (4.5 g) and DMSO (100 ml) at 90° for 4 hr. The mixture was poured into water, extracted with Et_2O. The extracts were washed with water and dried over $CaCl_2$. Distillation of the residue gave **3** (10.4 g, 97.8%), b.p.$_{40}$ 45°, n_D^{20} 1.5282. $M^{+\cdot}$ 86 (lit.:[28] b.p.$_{90}$ 60°, n_D^{20} 1.5284). ^1H NMR was discussed in Ref. 9a.

Reaction of acetylene with Se–KOH–DMSO triad. A mixture of powdered selenium (15.8 g), KOH (33.6 g), H_2O (10 ml) and DMSO (200 ml) was heated (110–120°) in a 2 l steel rotating autoclave for 5 hr under the acetylene pressure (initial—12 atm, residual—2 atm, 46 l of C_2H_2 in total). The reaction mixture was distilled in vacuum to collect 21.7 g of products including 2 g of water in the cooled trap. The organic layer was dried over K_2CO_3 and distilled in vacuum to give 12 g of **6** (20% yield, based on acetylene consumed) and 4.6 g (26%) of **7**, b.p.$_{720}$ 110°, n_D^{20} 1.5390, $M^{+\cdot}$ 132 (lit.[27] b.p.$_{760}$ 103–104°, n_D^{20} 1.5385). ^1H NMR (CCl_4): 5.51 and 5.72 (=CH_2, dd, J_{cis} = 9.4, J_{trans} = 17.9), 6.68 (=CH, q). IR spectrum: 1585 (νC=C), 3005, 3035, 3090 (ν=CH_2, =CH), 890 (δ=CH_2), 955, 1260 (δ=CH), 555 (νC–Se).

2-Vinyloxy-1,3-butadiene **6**. A mixture of H_2O (1.8 ml), KOH (1.68 g), $K_3PO_4{\cdot}7H_2O$ (6.76 g) and DMSO (200 ml) was heated (120–130°) in a 1 l steel rotating autoclave for 2.5 hr under acetylene pressure (initial—14 atm, residual—6 atm, 27 l of C_2H_2 in total). The reaction mixture was distilled to give 9 g of the run with b.p.$_{720}$ 70–90° consisting of 7 g of **6** (77% yield, based on the acetylene consumed) and 1.5 g of benzene. P glc-purified **6**: b.p.$_{720}$ 83°, d_4^{20} 0.8308, n_D^{20} 1.4596, $M^{+\cdot}$ 96. ^1H NMR and IR spectra were discussed in Ref. 5.

Reaction of acetylene with Te–KOH–HMPA triad. A mixture of Te (19.2 g), KOH (16.8 g), H_2O (8 ml) and HMPA (165 ml) was heated (110–120°) in a 1 l steel autoclave under initial acetylene pressure of 10 atm (21 l of C_2H_2 in total) for 6 hr. The reaction mixture was distilled to give 11.1 g of **8** (54.3%, based on the eq.: $4\,Te^0 \rightarrow 3\,Te^{2-} + Te^{6+}$), b.p.$_{720}$ 131–132°, d_4^{20} 1.7065, n_D^{20} 1.6120. ^1H NMR (CCl_4, TMS): 7.05 (=CH, q), 6.30 and 5.84 (=CH_2, dd, J_{cis} = 10.2, J_{trans} = 17.6). IR spectrum: 1572 (νC=C), 2928, 2985, 3018, 3066 (ν=CH_2, =CH), 905, 962, 1230, 1370 (δ CH_2, =CH), 515, 550 (νC–Te). (Found: C, 25.95; H, 3.22; Te, 70.18. Calc. for C_4H_6Te: C, 26.44; H, 3.33; Te, 70.23%).

Reaction of vinylacetylene with Se_8–KOH–DMSO triad. Vinylacetylene (32.6 g) was bubbled through a suspension consisting of Se_8 (16.7 g), KOH (17.4 g), H_2O (7.9 g) and DMSO (100 ml) at 110° for 6 hr. The reaction mixture was poured into water and extracted with Et_2O. The extracts were washed with water, dried over $CaCl_2$ and after the solvent removal, distilled in vacuum to give the run (6 g) with b.p.$_5$ 25–110° of the following composition (glc): 0.5 g of **12** (0.8% basing on vinylacetylene), 0.1 g (0.5%) of **9**, 1.4 g (5.4%) of **11**, 4.6 g (17.6%) of **10** and 0.1 g (0.4%) of **13**. Compounds **9**–**13** were isolated by P glc. The cis:trans ratio of **12** is 9:1 (^1H NMR).[14] NMR (^{13}C and ^{77}Se) spectra of **9** were discussed in Ref. (14). **11**, n_D^{20} 1.5760, NMR (^1H, ^{13}C) spectra were discussed in Ref. 9b, **10**, b.p.$_5$ 100°, n_D^{20} 1.6150, $M^{+\cdot}$ 186.[17] IR spectrum: 618 (ν C–Se), 1570, 1620 (ν C=C), 910 (overtone 1820), 998, 1310, 1420 (δ =CH, =CH_2), 3010 (ν =CH), 3090 (ν =CH_2). The NMR spectra were discussed in Ref. 16. (Found: C, 51.44; H, 5.34; Se, 42.90. Calc. for $C_8H_{10}Se$: C, 51.92; H, 5.40; Se, 42.67%). **13** (the cis-trans ratio 1:1), $M^{+\cdot}$ 194.[14] NMR (^1H, ^{13}C) and IR spectra were discussed in Ref. 14.

Reaction of vinylacetylene with Te–KOH–DMSO triad. A mixture of Te (25.9 g), KOH (20 g), H_2O (10.9 ml) and DMSO (100 ml) was heated (110°) with vinylacetylene (31.7 g) in a 1 l steel rotating autoclave for 3 hr. The reaction mixture was poured into water, and extracted with Et_2O. The extracts were washed with H_2O, the solvent was stripped off and the residue was distilled in vacuum to collect the run with b.p.$_4$ 80–86° (2.2 g) consisting of **14** (1.1 g). After P glc isolation it has n_D^{20} 1.6310, $M^{+\cdot}$ 236. IR spectrum: 605 (ν C–Te), 907 (overtone 1814), 988 (δ =CH), 1564, 1623 (ν C=C), 3090 (ν =CH_2). NMR (^1H, ^{13}C) in agreement with the data in Ref. 14.

Reactions in the Se–KOH–DMSO system. A suspension of Se (28.4 g), KOH (25.9 g), H_2O (11.6 ml), and DMSO (100 ml) was heated (110°) with stirring for 6 hr, volatile products being trapped at −40°. The reaction mixture was poured into water and extracted with Et_2O. The extracts were washed with H_2O and dried over $CaCl_2$, then the solvent was removed. The residue (6.1 g) was shown (glc) to consist of 4.4 g (3.3%) of dimethyl disulfide, 0.5 g (0.2%) of dimethyl diselenide, 1.0 g (0.5%) of dimethyl sulfoselenide **15**, and 0.2 g (0.1%) of methyl methylthiomethyl selenide **16**. Among the products trapped 7.2 g (8.2%) of dimethyl sulfide was identified. The yields (figures in parenthesis) were estimated based on the DMSO taken. The mass and NMR spectra of the products (isolated by P glc) were in agreement with data in Ref. 29.

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