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Chlorochalcogenation of Acetylenes with Benzenesulfen- (or selenen)amides and Tin(IV) Chloride

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Abstract—Benzenesulfenamides and benzeneselenenamides reacted with terminal and internal acetylenes (hex-1-yne, phenylacetylene, hex-3-yne, but-2-yne-1,4-diol, and diphenylacetylene) in the presence of $SnCl_4$ to give the corresponding chloroethenyl sulfides and selenides. From symmetric acetylenes, only *E* isomers (*E*)-ArXCR=CClR (X = S, Ar = Ph, 4-ClC_6H_4; R = Et, Ph, $HOCH_2$; X = Se, Ar = Ph, R = Et) were formed. The reactions of benzenesulfenamide with terminal acetylenes, apart from the corresponding Markownikoff and anti-Markownikoff adducts (PhSCH=CClR and PhSCR=CHCl, R = Bu, Ph) gave ethynyl sulfides PhSC≡CR (R = Ph, Bu) and *cis*/*trans*-isomeric 1,2-bis(phenylsulfanyl)chloroethenes PhSCR=CClSPh (R = Ph, Bu). The results were interpreted assuming intermediate generation of sulfenyl and selenenyl chlorides via reaction of sulfen- and selenenamides with $SnCl_4$.

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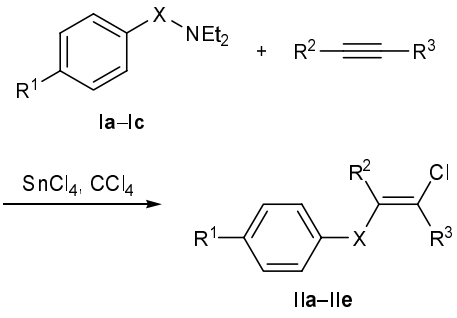
Sulfenyl- and selenenylhalogenation of acetylenic compounds with organylsulfenyl halides and organylselenenyl halides is one of the most extensively studied methods of synthesis of 2-haloalkenyl sulfides and selenides. However, sulfenyl and selenenyl halides are fairly unstable compounds which are readily converted into the corresponding disulfides and diselenides on exposure to air. On the other hand, it was recently shown that stable sulfenamides or sulfenanilides in the presence of hydrobromic acid [1] and such Lewis acids as zinc, magnesium, antimony, and tin iodides [2] or phosphoryl halides [3] are synthetic equivalents of sulfenyl halides and that their reactions with alkenes and alkynes lead to sulfenylhalogenation products. The reactions with alkenes yield 2-iodo(bromo)alkyl sulfides [1, 2], while terminal and disubstituted acetylenes give rise to mixtures of the corresponding *syn* and *anti* adducts formed both according to the Markownikoff rule and opposite to it [1, 3]. Apart from sulfenyl halides, initial compounds for the synthesis of sulfenamides may be selenocyanates, selenenic acids [4], sulfenic acid esters, and dialkyl or diaryl disulfides [5]; therefore, chalcogenamides become a promising and convenient alternative to unstable chalcogenyl halides.

We have revealed a new chalcogenohalogenating system which consists of equimolar amounts of sulfen- or selenenamide **Ia**–**Ic** and tin(IV) chloride. The synthetic potential of this system was examined using terminal and disubstituted acetylenes: hex-1-yne, phenylacetylene, hex-3-yne, but-2-yne-1,4-diol, and diphenylacetylene. The reactions with symmetric acetylenes was stereoselective, and the products were exclusively (*E*)-2-chloroethenyl sulfides **IIa**–**IId** and selenide **IIe** (Scheme 1). Their *trans* configuration follows from complete similarity of the ^1H and ^{13}C NMR spectra of adducts **IIa** and **IId** and the product obtained by electrophilic addition of benzenesulfenyl chloride (**IV**) to hex-3-yne in methylene chloride

Scheme 1.



I, X = S, R^1 = H (**a**), 4-Cl (**b**); X = Se, R^1 = Ph (**c**); **II**, X = S, R^1 = Ph, R^2 = R^3 = Et (**a**), Ph (**b**), CH_2OH (**c**); X = S, R^1 = 4-Cl, R^2 = R^3 = Et (**d**); X = Se, R^1 = Ph, R^2 = R^3 = Et (**e**).

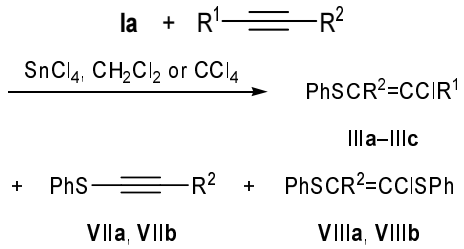
(the latter process is known to occur as *anti* addition) [3, 6–8]. In particular, the methylene carbon atom in position *5* of the hex-3-ene chain in *trans* adducts **IIa** and **IId** appears in the ^{13}C NMR spectra in a weaker field (δ_C 27.8 ppm) as compared to the corresponding *cis* adducts (δ_C 24.4 ppm) [8].

Benzenesulfenamide (**Ia**) failed to react with acetylene in the presence of $SnCl_4$ under atmospheric pressure. From the reaction mixture we isolated only diphenyl disulfide (**Va**) which was formed via hydrolysis of benzenesulfenyl chloride (**IV**).

According to the ^1H NMR data, the reaction of benzeneselenenamide (**Ic**) with hex-3-yne and $SnCl_4$ gave 3-chloro-4-(phenylselanyl)hex-3-ene (**IIe**) and *N*-[dichloro(phenyl)-λ^4-selanyl]-*N*-methylmethanamine (**VI**); the chemical shifts of the ethyl protons in **VI** differed from those typical of initial selenenamide **Ic** but coincided with the chemical shifts calculated for $PhSeCl_2NEt_2$. During chromatographic separation, dichloride **VI** decomposed to diphenyl diselenide (**Vb**), and only the latter and selenide **IIe** were detected in the mass spectrum of the mixture (GC–MS data).

Three types of products were formed in the reactions of benzenesulfenamide (**Ia**) with phenylacetylene and hex-1-yne: 2-chloroethenyl sulfides **IIIa**–**IIIc**, ethynyl phenyl sulfides **VIIa** and **VIIb**, and isomeric 1,2-bis(phenylsulfanyl)chloroethenes **VIIIa** and **VIIIb** (Scheme 2); these compounds were identified by the ^1H NMR spectra and GC–MS data. In the reaction with phenylacetylene, the 1 : 1 adduct was formed as a single isomer (*E*-**IIIa**), while in the reaction with hex-1-ynes, the ratio of regioisomeric sulfides *E*-**IIIb** and *E*-**IIIc** was 3 : 2.

Scheme 2.

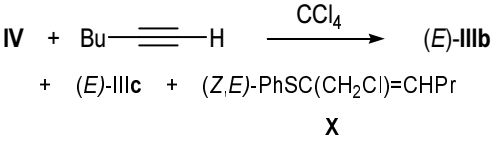


III, R^1 = H, R^2 = Ph (**a**), Bu (**b**); R^1 = H, R^2 = Bu (**c**); **VII**, **VIII**, R^1 = Ph (**a**), Bu (**b**).

Sulfide **IIIa** is the *E* isomer of the Markownikoff adduct. Its configuration follows from the fact that compound **IIIa** undergoes dehydrochlorination to ethynyl sulfide **VIIa** by the action of potassium *tert*-butoxide in *tert*-butyl alcohol and does not by the action of triethylamine. It is known that only such strong bases as potassium *tert*-butoxide in *tert*-butyl alcohol and KOH in DMSO are capable of effecting *syn*-dehydrochlorination of compounds like **IIIa** [9]. The anti-Markownikoff adduct, sulfide *E*-**IIId**, was obtained by electrophilic addition of benzenesulfenyl chloride **IV** to phenylacetylene in CCl_4 [10]; the vinyl proton signal in its ^1H NMR spectrum is located in a stronger field (see Experimental). The difference in the regioselectivity of the above processes may be attributed to the different acidities of the reaction media: according to [10], increased acidity favors formation of the Markownikoff adduct. Zyk et al. [3] erroneously assigned the structure of 2-chloro-1-phenylethenyl phenyl sulfide PhSC(Ph)=CHCl (*E*-**IIId**) to a compound whose ^1H NMR spectrum was identical to that of adduct **IIIa**.

The configuration of sulfides **IIIb** and **IIIc** was determined by comparison with the products obtained by chlorosulfenylation of hex-1-yne with benzenesulfenyl chloride (**IV**); this reaction follows the *anti*-addition pattern and gives both Markownikoff and anti-Markownikoff adducts [8, 10]. We found that the reaction with sulfenyl chloride **IV** is accompanied by isomerization of anti-Markownikoff adduct *E*-**IIIc** into *Z* and *E* isomers of 1-chloro-2-(phenylsulfanyl)hex-2-ene (**X**) (Scheme 3).

Scheme 3.



No isomerization was observed in the reaction with benzenesulfenamide (**Ia**). As in the reaction with phenylacetylene, treatment with an alcoholic alkali or potassium *tert*-butoxide in *tert*-butyl alcohol of the product mixture obtained from hex-1-yne and benzenesulfenamide resulted in dehydrochlorination of both isomers with formation of hex-1-yn-1-yl sulfide **VIIb**. However, the dehydrochlorination was accompanied by isomerization of sulfide **VIIb** into hex-2-yn-1-yl phenyl sulfide $PhSCH_2C{\equiv}CPr$ (**XI**), as followed from the GC–MS data (two compounds with equal molecular weights were present) and ^1H NMR spectra which contained a triplet at δ 3.61 ppm ($^5J_{HH}$ = 2.3 Hz) due to bridging $SCH_2C{\equiv}$ methylene group. Sulfide *E*-**IIIb** (major product) undergoes dehydrochlorination by the action of potassium *tert*-butoxide to a greater extent, which is consistent with its *E* configuration and Mar-

kownikoff adduct structure. The fact that anti-Markownikoff adduct *E*-**IIIc** also undergoes dehydrochlorination indicates isomerization of anti-Markownikoff adducts obtained from alkylacetylenes into Markownikoff adducts.

The above data led us to conclude that the examined reactions of sulfen- and selenenamides with acetylenic compounds in the presence of $SnCl_4$ involve intermediate formation of the corresponding sulfenyl and selenenyl chlorides via chlorination of chalcogenamides **Ia**–**Ic**. According to the GLC and ^{1}H NMR data, treatment of benzenesulfenamide (**Ia**) with $SnCl_4$ gives sulfenyl chloride **IV** and diphenyl disulfide. The subsequent electrophilic *anti*-addition of sulfenyl or selenenyl chloride to alkynes leads to 2-chloroethenyl sulfides or selenides **IIa**–**IIe** and **IIIa**–**IIIc**. The reaction with terminal acetylenes is accompanied by dehydrochlorination of sulfides **IIIa** and **IIIb** to give the corresponding ethynyl sulfides **VIIa** and **VIIb** due to the presence in the reaction mixture of compounds having an amino group. The addition of sulfenyl chloride **IV** to ethynyl sulfides **VIIa** and **VIIb** results in formation of chloroethenes **VIIIa** and **VIIIb**.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured from 5–10% solutions in $CDCl_3$ on a Bruker DPX-400 spectrometer at 400 and 100.61 MHz, respectively. The mass spectra (electron impact, 70 eV) were recorded on an HP 5971A mass-selective detector coupled with an HP 5890 chromatograph (Ultra-2 capillary column, 20 m; stationary phase 5% phenylmethylsilicone; oven temperature 70–280°C).

Initial *N*,*N*-diethylarenesulfenamides **Ia** and **Ib** and *N*,*N*-diethylbenzeneselenenamide (**Ic**) were synthesized by reaction of the corresponding sulfenyl or selenenyl chloride with diethylamine [11, 12].

3-Chloro-4-(4-chlorophenylsulfanyl)hex-3-ene (IId). *N*,*N*-Diethyl-*p*-chlorobenzenesulfenamide (**Ib**), 906 mg (5 mmol), and tin(IV) chloride, 1303 mg (5 mmol), were mixed at 0°C under argon, the mixture was stirred for 0.5 h, 854 mg (10 mmol) of hex-3-yne was added, and the mixture was stirred for 26 h at room temperature. The mixture was then treated with water to remove excess $SnCl_4$ and extracted with diethyl ether. Removal of the solvent from the extract gave 789 mg (70%) of a mixture containing (according to the GC–MS data) 87% of compound **IId,** 7% of 3-chloro-4-(phenylsulfanyl)hex-3-ene (**IIa**) (due to the presence of an impurity of sulfenamide **Ia** in initial sulfenamide **Ib**), 2.5% of bis(*p*-chlorophenyl) disulfide (**Vc**), and 3.5% of bis(*o*-chlorophenyl) disulfide (**Vd**). ^{1}H NMR spectra, δ, ppm (*J*, Hz): *E*-**IIa**: 7.28–7.14 m (5H, C_6H_5), 2.79 q (2H, CH_2, $^3J_{HH}$ = 7.4), 1.13 t (3H, CH_3, $^3J_{HH}$ = 7.5) (EtCCl=), 2.38 q (2H, CH_2, $^3J_{HH}$ = 7.4), 1.03 t (3H, CH_3, $^3J_{HH}$ = 7.5) [EtC(SAr)=]; *E*-**IId**: 7.13 d and 7.23 d (4H, C_6H_4, $^3J_{HH}$ = 8.45), 2.77 q (2H, CH_2, $^3J_{HH}$ = 7.3), 1.13 t (3H, CH_3, $^3J_{HH}$ = 7.3) (EtCCl=), 2.37 q (2H, CH_2, $^3J_{HH}$ = 7.3), 1.03 t (3H, CH_3, $^3J_{HH}$ = 7.4) [EtC(SAr)=]; published data [8]: ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.80 q and 1.12 t (EtCCl=), 2.40 q and 1.04 t [EtC(SAr)=]; *Z* isomer: 2.48 q and 1.16 t (EtCCl=), 2.21 q and 1.08 t [EtC(SAr)].

The ^{13}C NMR spectrum of adduct **IId** coincided with that reported in [8] for the *trans* isomer of **IId** [8].

Mass spectra, *m*/*z* (^{35}Cl; I_{rel}, %): **IId**: 260 (100) M^+, 224 (22.5) $[M - HCl]^+$, 209 (38.3) $[M - HCl - Me]^+$, 143 (37.4) $[ClC_6H_4S]^+$, 108 (60.3) $[C_6H_4S]^+$; **IIa**: 226 (100) M^+, 190 (28.5) $[M - HCl]^+$, 175 (56.1) $[M - HCl - Me]^+$, 109 (48.3) $[C_6H_5S]^+$; **Vc**, **Vd**: 286 (57.1) M^+, 143 (100) $[ClC_6H_4S]^+$, 108 (61.1) $[C_6H_4S]^+$.

3-Chloro-4-(phenylselanyl)hex-3-ene (IIe). Following an analogous procedure, the reaction of 0.23 g (1 mmol) of benzeneselenenamide (**Ic**) with 0.16 g (2 mmol) of hex-3-yne and 0.26 g (1 mmol) of $SnCl_4$ in 10 ml of CCl_4 (reaction time 6 h; after treatment with water, the mixture was extracted with chloroform) gave 0.23 g of a ~1:1 mixture of compound **IIe** (42%; 84% on the reacted **Ic**) and $PhSeCl_2NEt_2$ (**VI**). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): *E*-**IIe**: 7.30–7.21 m (5H, C_6H_5), 2.79 q (2H, CH_2, $^3J_{HH}$ = 7.4), 1.11 t (3H, CH_3, $^3J_{HH}$ = 7.3) (EtCCl=), 2.44 q (2H, CH_2, $^3J_{HH}$ = 7.4), 1.02 t (3H, CH_3, $^3J_{HH}$ = 7.3) [EtC(SeAr)=]. Mass spectra, *m*/*z* (^{35}Cl, ^{80}Se; I_{rel}, %): **IIe**: 274 (100) M^+, 157 (58.8) $[PhSe]^+$, 143 (12.0) $[ClCH{=}CHSe]^+$, 117 (26.8) $[M - PhSe]^+$, 77 (80.9) $[Ph]^+$; **Vb**: 314 (81.6) M^+, 234 (19.7) $[PhSePh]^+$, 157 (100) $[PhSe]^+$, 77 (74.6) $[Ph]^+$.

2-Chloro-3-(phenylsulfanyl)but-2-ene-1,4-diol (IIc). Likewise, from 1.22 g (6.73 mmol) of benzenesulfenamide (**Ia**), 1.75 g (6.73 mmol) of $SnCl_4$ in 20 ml of CCl_4, and 0.58 g (6.73 mmol) of but-2-yne-1,4-diol in 40 ml Et_2O (reaction time 9 h; the reaction mixture was washed with water and extracted with chloroform–ethanol–diethyl ether) we obtained 1.17 g of a mixture which contained (according to the GC–MS data) 48% (37% on the initial sulfenamide **Ia**) of diol **IIc** and 43% of diphenyl disulfide **Va** (43%). ^{1}H NMR spectrum of *E*-**IIc**, δ, ppm: 4.30 s (2H, CH_2CCl=), 4.60 s [2H, $CH_2C(SAr)$=], 7.23–7.56 m (5H, C_6H_5). Mass spectrum of **IIc**, *m*/*z* (^{35}Cl; I_{rel}, %):

230 (15.2) M^+, 211 (9.9) $[M - H_3O]^+$, 177 (12.8) $[M - Cl - H_2O]^+$, 147 (18.6) $[PhSC{\equiv}CCH_2]^+$, 134 (14.9) $[M - Ph - H_3O]^+$, 110 (100) $[PhSH]^+$, 103 (11.9) $[PhCH{=}CH]^+$, 91 (14.1) $[PhCH_2]^+$, 77 (38.6) $[Ph]^+$.

Reaction of *N*,*N*-diethylbenzenesulfenamide (Ia) with hex-1-yne in the presence of $SnCl_4$. The reaction was carried out using 1.81 g (10 mmol) of sulfenamide **Ia**, 2.61 g (10 mmol) of $SnCl_4$, and 1.64 g (20 mmol) of hex-1-yne in 20 ml of CCl_4; reaction time 5 h; the mixture was treated with water and extracted with chloroform and diethyl ether to obtain 1.56 g of a mixture which contained (according to the GC–MS data), 18% of hex-1-yn-1-yl phenyl sulfide (**VIIb**), 28% of (*E*)-2-chloro-1-(phenylsulfanyl)hex-1-ene (*E*-**IIIb**), 18% of (*E*)-1-chloro-2-(phenylsulfanyl)-hex-1-ene (*E*-**IIIc**), 27 and 4.5% of isomeric 1-chloro-1,2-bis(phenylsulfanyl)hex-1-enes **VIII**, and 4.5% of diphenyl disulfide (**Va**). ^{1}H NMR spectra, δ, ppm (*J*, Hz): *E*-**IIIb**: 7.48 d ($^3J_{HH}$ = 7.3), 7.40–7.17 m (5H, C_6H_5), 6.30 s (1H, ArSCH=), 2.40 t (2H, $^3J_{HH}$ = 7.9), 1.60–1.18 m, (4H, CH_2CH_2), 0.87 t ($^3J_{HH}$ = 7.3) and 0.79 t ($^3J_{HH}$ = 7.4) (3H, CH_3); *E*-**IIIc**: 7.48 d (*J* = 7.3) and 7.40–7.17 m (5H, C_6H_5), 6.23 s (1H, =CHCl), 2.33 t (2H, $^3J_{HH}$ = 7.5), 1.60–1.18 m (4H, CH_2CH_2), 0.87 t ($^3J_{HH}$ = 7.3) and 0.79 t ($^3J_{HH}$ = 7.4) (3H, CH_3). Mass spectra, *m*/*z* (^{35}Cl; I_{rel}, %): **IIIb**: 226 (44.4) M^+, 183 (21.3) $[M - Pr]^+$, 147 $[PhSC_3H_2]^+$ (100), 134 (8.7) $[PhSC{\equiv}CH]^+$, 109 (25.6) $[PhS]^+$, 77 (35.3) $[Ph]^+$; **IIIc**: 226 (28.7) $[M]^+$, 191 (11.0) $[M - HCl]^+$, 184 (17.5) $[M - C_3H_8]^+$, 161 (5.8) $[PhSC{\equiv}CCH_2CH_2]^+$, 149 (38.3) $[M - Ph]^+$, 135 (87.7) $[PhSCH{=}CH]^+$, 109 (50.4) $[PhS]^+$, 77 (36.9) $[Ph]^+$; **VIIb**: 190 (40.7) M^+, 161 (6.2) $[M - Et]^+$, 147 (38.9) $[M - Pr]^+$, 128 (10.3) $[PhC{\equiv}CCH{=}CH_2]^+$, 103 (99.0) $[SC_5H_{11}]^+$, 77 (88.8) $[Ph]^+$; **VIIIb**: 334 (61.7) M^+, 181 (51.0) $[M - PhS - C_3H_8]^+$, 169 (9.1) $[M - PhS - C_4H_8]^+$, 147 (82.0) $[M - PhSH - Ph]^+$, 134 (11.8) $[PhSC{\equiv}CH]^+$, 109 (68.7) $[PhS]^+$, 77 (96.0) $[Ph]^+$.

A 0.23-g portion of the product mixture was heated for 1 h with 0.25 g of potassium *tert*-butoxide in 15 ml of *tert*-butyl alcohol under reflux. The solution was poured into water and extracted with diethyl ether, and the extract was dried over $CaCl_2$ and evaporated to obtain 0.23 g of a mixture containing (according to the GC–MS data) 12% of hex-1-yn-1-yl phenyl sulfide (**VIIb**), 15.5% of hex-2-yn-1-yl phenyl sulfide $PhSCH_2C{\equiv}CPr$ (**XI**), 3.5% of (*E*)-2-chloro-1-(phenylsulfanyl)hex-1-ene (*E*-**IIIb**), 4% of (*E*)-1-chloro-2-(phenylsulfanyl)hex-1-ene (*E*-**IIIc**), and 36 and 8% of isomeric 1-chloro-1,2-bis(phenylsulfanyl)hex-1-enes **VIIIb**.

Reaction of *N*,*N*-diethylbenzenesulfenamide (Ia) with phenylacetylene in the presence of $SnCl_4$. The reaction was carried out in a similar way using 0.90 g (5 mmol) of sulfenamide **Ia**, 1.30 g (5 mmol) of $SnCl_4$, and 1.02 g (10 mmol) of phenylacetylene in 15 ml of methylene chloride; reaction time 14 h; the mixture was treated with water and extracted with chloroform to obtain 0.83 g of a mixture containing (according to the GC–MS data) 16.5% of 2-phenylethynyl phenyl sulfide (**VIIa**), 49% of (*E*)-2-chloro-2-phenylethenyl phenyl sulfide (**IIIa**), and 11 and 19% of isomeric 1-chloro-2-phenyl-1,2-bis(phenylsulfanyl)ethenes **VIIIa**. ^{1}H NMR spectrum of (*E*-**IIIa**), δ, ppm: 7.02–7.85 m (10H, $2C_6H_5$), 6.68 s (1H, ArSCH=); published data [13]: ^{1}H NMR spectrum: δ 6.67 ppm. Mass spectra, *m*/*z* (^{35}Cl, I_{rel}, %): **IIIa**: 246 (64.7) M^+, 211 (52.4) $[M - Cl]^+$, 178 (47.5) $[PhC{\equiv}CPh]^+$, 134 (37.7) $[M - Ph - Cl]^+$, 109 (23.2) $[PhS]^+$, 77 (98.5) $[Ph]^+$; **VIIa**: 210 (100) M^+, 178 (13.4) $[PhC{\equiv}CPh]^+$, 165 (53.0) $[PhCHPh]^+$, 77 (43.1) $[Ph]^+$; **VIIIa**: 354 (34.7) M^+, 244 (12.2) $[M - PhSH]^+$, 210 (100) $[PhSC{\equiv}CPh]^+$, 178 (14.0) $[PhC{\equiv}CPh]^+$, 165 (42.8) $[C_6H_4CHC_6H_4]^+$, 109 (68.1) $[PhS]^+$, 77 (59.2) $[Ph]^+$.

A 0.15-g portion of the product mixture was heated with 0.15 g of potassium *tert*-butoxide in 10 ml of *tert*-butyl alcohol for 13 h under reflux. The solution was poured into water and extracted with diethyl ether, and the extract was dried over $CaCl_2$ and evaporated to obtain 0.13 g of a mixture containing (according to the GC–MS data) 38.5% of 2-phenylethynyl phenyl sulfide (**VIIa**), 1.5% of (*E*)-2-chloro-2-phenylethenyl phenyl sulfide (**IIIa**), and 16.5, 30.5, and 6% of isomeric chloro(phenyl)bis(phenylsulfanyl)ethenes **VIIIa**.

(*E*)-3-Chloro-4-(phenylsulfanyl)hex-3-ene (IIa). A solution of 1.04 g (7.18 mmol) of benzenesulfenyl chloride (**IV**) in 2 ml of methylene chloride was added dropwise at room temperature to a solution of 0.59 g (7.18 mmol) of hex-3-yne in 2 ml of CH_2Cl_2, and the mixture was stirred for 4 h. Removal of the solvent left 1.60 g (98%) of compound **IIa**. The ^{1}H NMR spectrum of the product was identical to that given above. ^{13}C NMR spectrum, δ_C, ppm: 130.0 [=C(S)], 141.0 (=CCl), 12.2 (C^6), 27.9 (C^5), 31.0 (C^2), 12.9 (C^1).

2-Chloro-1-phenylethenyl phenyl sulfide (IIId). A solution of 2.04 g (20 mmol) of phenylacetylene in 10 ml of carbon tetrachloride was added dropwise under argon to 1.44 g (10 mmol) of benzenesulfenyl chloride (**IV**) in 10 ml of carbon tetrachloride, and the bright orange mixture was stirred for 5 h until it became colorless. The solvent was removed to leave

2.28 g (92.5%) of sulfide *E*-**IIId** containing (according to the ^{1}H NMR data) an impurity of chloroethene *E*-**IIIa** (6%). ^{1}H NMR spectrum, δ, ppm: 7.14–7.61 m (10H, $2C_6H_5$), 6.59 s (1H, =CHCl).

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