Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 708–712. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 773–777.

Reaction of the System Arene(Hetarene)thiol–Diselenide with Phenylacetylene

L. K. Papernaya, A. I. Albanov, E. N. Sukhomazova,
E. P. Levanova, and E. N. Deryagina

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia

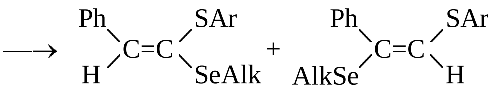
Received April 15, 2002

Abstract—Liquid-phase thermal reactions of phenylacetylene with the system arene(hetarene)thiol–diselenide at 110–180°C proceed through conjugate addition to the phenylacetylene triple bond of one alkylselanyl and one arene(hetarenesulfanyl groups to form 2-alkylselanyl-2-[aryl(hetaryl)sulfanyl]-1-phenylethenes and 1-alkylselanyl-2-[aryl(hetaryl)sulfanyl]-1-phenylethenes. Therewith, direct addition of thiols to phenylacetylene slows down.

Earlier we studied the thermal reactions of phenylacetylene with mixtures of thiophenol with dialkyl diselenides, involving simultaneous addition to the phenylacetylene triple bond of alkylselanyl and phenylsulfanyl groups. The reaction products were identified as mixtures of (*E*)- and (*Z*)-2-alkylselanyl-1-phenyl-1-phenylsulfanylethenes [1].

Proceeding with the research into thermal reactions involving chalcogenyl radicals, we brought into reaction with phenylacetylene other combinations of thiols with diselenides. The reactions of phenylacetylene with the arene(hetarene)thiol–dialkyl diselenide system occur at 110–180°C and result in conjugate addition to the triple bond of one sulfanyl and one selanyl group. Detailed ^{1}H and ^{13}C NMR analysis allowed us to identify the reaction products, including those obtained in [1], and assign another structure to them. Reaction (1) provides two types of previously unknown types of isomeric compounds, 2-alkylselanyl-1-phenyl-2-(phenylsulfanyl)ethenes **I** and 1- alkylselanyl-1-phenyl-2-(phenylsulfanyl)ethenes **II**.

$$PhC{=}CH + ArSH + Alk_2Se_2$$


(1)

Ia–**Ic** **IIa**–**IIc**

Ar = Ph (**Ia, IIa**), *p*-Tol (**Ib, IIb**), 2-thienyl (**Ic, IIc**); Alk = Me, Et, Pr, Bu.

Apart from thiophenol, reaction (1) was performed with 4-methylthiophenol and 2-thiophenethiol. The reaction conditions and product yields are listed in Table 1. Most commony, reaction (1) at 110–180°C is complete within 0.5–1.0 h. By varying reactant ratios and temperature we could bring the yields of compounds **Ia**–**Ic** and **IIa**–**IIc** to 30–40% per taken phenylacetylene. With 4-methylthiophenol and 2-thiophenethiol, the product yields are higher. Higher yields are favored by using molar excesses of phenylacetylene and dialkyl diselenides, as well as dialkyl deselenides with a shorter alkyl chain.

The major products of reaction (1) are compounds **Ia**–**Ic**. Compound **Ia** is formed the most selectively. Whereas with the diselenide–thiophenol or diselenide–2-thiophenethiol systems the **Ia** : **IIa** and **Ic** : **IIc** ratios are 3 : 1, the **Ib** : **IIb** ratio resulting from the reaction of phenylacetylene with the diselenide–4-methylthiophenol system is 4 : 3.

Mechanistically, reaction (1) apparently involves thermal generation of alkylselanyl radicals from diselenides. The selanyl radicals effect hydrogen transfer from thiol to form arylsulfanyl radicals [2]. The arylsulfanyl radicals initially add to the β position of the phenylacetylene triple bond with subsequent stabilization as radical adducts **III**. The latter are further stabilized in two ways: (a) by transferring the alkylselanyl group from dialkyl diselenide both to the α and β position of the double bond, forming compounds **I** and **II** by scheme (2); and (b) by transferring a hydrogen atom exclusively to the α position of the phenylacetylene triple bond, forming compounds **IV** in 3–55 % yields by scheme (3).

The yield of compounds **IV** in reaction (3) with 2-thiophenethiol is lower. The *E/Z* ratio decreases in the series thiophenol, 4-methylthiophenol, 2-thiophenethiol (Table 1). With thiophenol, the *E* isomer of **IV** forms almost exclusively. The direct reaction

1070-3632/04/7405-0708 ©2004 MAIK “Nauka/Interperiodica”

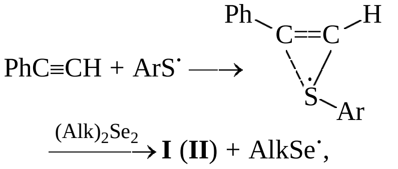
Table 1. Reaction of phenylacetylene with the arenethiol (ArSH)–dialkyl diselenide (R_2Se_2) system

Temperature, °C	Reaction time, h	R	Ar	PhC≡CH : ArSH : R_2Se_2 molar ratio	Conversion, %		
					PhC≡CH	Alk_2Se_2	ArSH
140–180	0.5	C_3H_7	C_6H_5	4 : 2 : 1	81.1	89.0	100.0
140–180	0.5	C_3H_7	C_6H_5	4 : 2 : 1.5	83.5	59.0	100.0
140–150	1.5	C_3H_7	4-$CH_3C_6H_4$	2 : 2 : 1	95.5	87.2	81.0
140–160	1.0	C_3H_7	4-$CH_3C_6H_4$	2 : 2 : 1.5	100.0	69.6	79.0
140–170	1.0	C_3H_7	4-$CH_3C_6H_4$	3 : 2 : 1.5	79.5	89.6	72.1
140–180	0.5	CH_3	2-Thienyl	3 : 2 : 1.5	85.2	69.8	100.0
110–150	0.5	CH_3	"	3 : 2 : 1.5	88.9	83.0	100.0
130–150	0.5	C_3H_7	"	4 : 2 : 1.5	31.4	30.1	93.0
140–170	0.5	C_3H_7	"	3 : 2 : 1.5	74.0	38.1	100.0

Yield, % per taken (reacted) PhC≡CH			Product ratio		Yields of other reaction products, %
I, **II**	**IV**	**V**	**I**/**II**	**IV**, *E*/*Z*	
21.7 (26.7)	29.1 (35.8)	(8.9)	3/1	5/1	**VI** (5), Ph_2S_2 (traces)[a]
27.5 (32.7)	33.1 (39.0)	(11.1)	3/1	5/1	**VI** (5), Ph_2S_2 (2.5)[a]
16.9 (23.8)	55.8 (65.4)	Traces	4/3	4/1	–
39.6	44.2	(5.6)	4/3	4/1	–
35.6 (46.9)	34.2 (42.6)	(6.4)	4/3	4/1	–
31.5 (37.0)	9.8 (11.5)	(12.8)	4/3	3/1	**VI** (traces)[b]
38.4 (43.1)	10.1 (11.3)	(18.2)	4/3	3/1	**VI** (traces)[b]
14.3 (52.1)	3.5 (12.7)	(4.2)	3/1	3/1	**VI** (traces)[b]
26.5 (35.6)	6.2 (8.3)	(5.5)	3/1	3/1	**VI** (3)[b]

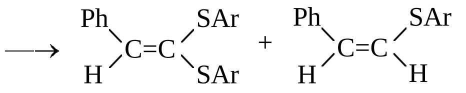
[a] 2,4-Diphenylthiophene and 2,5-diphenylselenophene are formed in trace amounts. [b] High-boiling unidentified products are also formed.

$$Alk_2Se_2 \rightleftarrows 2AlkSe^{\bullet} \overset{2ArSH}{\rightleftarrows} 2ArS^{\bullet} + 2AlkSeH$$



(2)

PhC=CH + ArSH



(3)

IVa–IVc

Ar = Ph (**a**), *p*-Tol (**b**), 2-thienyl (**c**).

of thiols with phenylacetylene was studied, resulting in quantitative formation of adducts **IV**. Unlike thiophenol and 4- methylthiophenol, 2-thiophenethiol very slowly reacts with phenylacetylene. The reaction at 100°C takes 40 min, involving a 100% conversion of the starting compounds and preferential formation of the *E* isomer.

Reaction (1), along with major products **I**, **II**, and **IV**, gives 2-alkylselanyl-1-phenylethenes **V** in 3–18% yields and 2-alkylselanyl-1-phenylethanes **VI** in trace amounts. These products are probably formed by the following schemes [1].

$$PhC{=}CH + AlkSe^{\bullet} \longrightarrow Ph\dot{C}{=}CHSeAlk,$$

$$Ph\dot{C}{=}CHSeAlk + PhSH \longrightarrow \underset{\textbf{V}}{PhCH{=}CHSeAlk} + PhS^{\bullet},$$

$$Ph\dot{C}{=}CHSeAlk + AlkSeH \longrightarrow \textbf{V} + AlkSe^{\bullet},$$

$$\textbf{V} \longrightarrow PhCH{=}\dot{C}H + AlkSe^{\bullet},$$

$$PhCH{=}\dot{C}H + ArSH \longrightarrow PhCH{=}CH_2 + ArS^{\bullet},$$

$$PhCH{=}CH_2 + AlkSe^{\bullet} \longrightarrow Ph\dot{C}HCH_2SeAlk,$$

$$Ph\dot{C}HCH_2SeAlk + ArSH \longrightarrow \underset{\textbf{VI}}{PhCH_2CH_2SeAlk} + ArS^{\bullet}.$$

Thiophenol is partially oxidized to diphenyl disulfide (yield up to 5%). At the same time, no cor-

Table 2. Characteristics of 2-alkylselanyl-2-arylsulfanyl-1-phenylethenes **I** and 1-alkylselanyl-2-arylsulfanyl-1-phenylethenes **II**

Comp. no.	^{80}Se (from mass spectrum)	bp, °C (p, mm)	^{1}H NMR spectrum, δ, ppm (J, Hz)	^{13}C NMR spectrum, δ_C, ppm (J, Hz)
Ia	334	180–195 (1–2)	1.08 t (3H, CH$_3$); 1.77 sextet (2H, CH$_2$C); 2.73 t (2H, CH$_2$Se); 7.06 s [1H, CH=, ^3J(^{77}Se–^{1}H) (SeC=CH) 10.3]; 7.2–7.8 m (10H, Ar)	14.28 (CH$_3$); 23.73 (CH$_2$); 29.14 [CH$_2$Se, ^1J(^{77}Se–^{13}C) 61.3]; 131.48 [CH=, ^2J(Se–C) 14.6]; 131.16 (=C); 130.20, 129.27, 128.52, 128.03 [C$_{o,m}$(Ph)]; 127.15, 126.58 [C$_p$(Ph)]; 139.93 [C$_i$(Ph)]; 135.53 [C$_i$(SPh)]
IIa	334	180–195 (1–2)	1.07 t (3H, CH$_3$); 1.78 sextet (2H, CCH$_2$); 2.69 t (2H, CH$_2$Se); 7.00 s [1H, CH=, ^3J(^{77}Se–^{1}H) (SeC=CH) 6.4]; 7.2–7.8 m (10H, Ar)	14.30 (CH$_3$), 23.36 (CH$_2$); 29.10 [CH$_2$Se, ^1J(^{77}Se–^{13}C) 64.4]; 125.66 [CH=, ^2J(Se–C) 22.2]; 130.60 (=C); 129.42, 129.32, 129.20, 128.35 [C$_{o,m}$(Ph)]; 127.60, 128.11 [C$_p$(Ph)]; 138.26 [C$_i$(Ph)]; 135.83 [C$_i$(SPh)]
Ib	349	202–204 (1–2)	0.9 s [3H, CH$_3$(Pr)]; 1.57 sextet (2H, CH$_2$); 2.31 s [3H, CH$_3$(Ar)]; 2.53 t (2H, CH$_2$Se), 6.84 s [1H, CH=, ^3J(^{77}Se–^{1}H) (SeC=CH) 10.6]; 7.0–7.6 m (9H, Ar)	14.53 [CH$_3$(Pr)]; 21.23 [CH$_3$(Ar)]; 23.97 (CH$_2$); 29.28 (CH2Se); 132.73 (CH=); 127.60 [C$_p$(Ph)]; 127.97 [C$_o$(Ph)]; 128.57 [C$_m$(Ph)]; 140.60 [C$_i$(Ph)]; 129.94 [C3,5(Ar)]; 130.65 [C^{2,6}(Ar)]; 132.47 [C$_i$(SAr)]; 137.24 [C^4(Ar)]; 129.18 (=C)
IIb	349	202–204	0.89 t [3H, CH$_3$(Pr)]; 1.60 sextet (2H, CH$_2$); 2.29 s [3H, CH$_3$(Ar)]; 2.48 t (2H, CH$_2$Se); 6.77 s [1H, CH=, ^3J(^{77}Se–^{1}H) (SeC=CH) 6.4]; 7.0–7.6 m (9H, Ar)	14.53 [CH$_3$(Pr)]; 21.23 [CH$_3$(Ar)]; 23.60 (CH$_2$); 29.32 (CH$_2$Se); 127.05 (CH=); 128.11 [C$_p$(Ph)]; 128.39 [C$_o$(Ph)]; 129.36 [C$_m$(Ph)]; 129.95 [C^{3,5}(Ar)]; 130.12 [C^{2,6}(Ar)]; 132.42 [C$_i$(SAr)]; 136.92 [C^4(Ar)]; 129.14 (=C)
Ic	340	185–196 (1–2)	0.89 t (3H, CH$_3$, 3J 7.46); 1.57 sextet (2H, CH$_2$, ^3J 7.3); 2.51 t (2H, CH$_2$Se, ^3J 7.2); 6.75 s (1H, CH=); 6.93 d.d [1H, H^4(Ar), $J_{4,5}$ 5.26, $J_{4,3}$ 3.55]; 7.16 d [1H, H^3(Ar), $J_{3,4}$ 3.55]; 7.30 d.d [1H, H^5 (Ar), $J_{5,4}$ 5.26, $J_{5,3}$ 1.22]; 7.25 m (3H, H$_{m,p}$); 7.43 d (2H, H$_o$)	14.11 (CH$_3$); 23.51 (CH$_2$); 29.03 [CH$_2$Se, ^1J(^{77}Se–^{13}C) 61.6]; 132.81 (CH=); 132.85 (=C); 139.59 [C$_i$(Ph)]; 128.16, 127.50 [C$_{o,m}$(Ph)]; 129.30 [C$_p$(Ph)]
IIc	340	185–196 (1–2)	0.86 t (3H, CH$_3$); 1.72 sextet (2H, CH$_2$); 2.44 t (2H, CH$_2$Se); 6.65 s (1H, CH=); 6.90 d.d [1H, H^4(Ar), $J_{4,5}$ 5.38, $J_{4,3}$ 3.67]; 7.06 d [1H, H^3(Ar), $J_{3,4}$ 3.67]; 7.03 d [1H, H^5(Ar)]; 7.33 m (3H, H$_{m,p}$), 7.46 d (2H, H$_o$)	13.97 (CH$_3$); 23.10 (CH$_2$), 28.90 [CH$_2$Se, ^1J(^{77}Se–^{13}C) 61.6]; 138.11 [C$_i$(Ph)]; 128.10, 127.33 [C$_{o,m}$(Ph)]; 128.85 [C$_p$(Ph)]

responding disulfides from 2-thiphenethiol and 4-methylthiophenol were not found. Thus, the direct reaction of arenethiols with phenylacetylene, that proceeds quantitatively upon their mixing, slows down in the presence of dialkyl diselenides. This fact is explained by the higher activity of dialkyl diselenides in chalcogenyl radical transfer reactions, we observed previously in disproportionation reactions in thiol–diselenide systems [2]. Compounds **I**, **II**, and **IV** were isolated by vacuum distillation as yellow thick oils or difficultly crystallized materials. Their structure was assessed by ^{1}H and ^{13}C NMR spectroscopy and gas chromatography–mass spectrometry. The NMR spectra are given in Tables 2 and 3.

The ^{1}H NMR spectra of compounds **Ia**–**Ic** and **IIa**–**IIc** contain signals of two isomers. The olefin proton signals have satellite signals split by spin–spin coupling with ^{77}Se. Signal assignment to isomers **Ia**–**Ic** and **IIa**–**IIc** was performed by the Se–H coupling

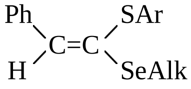
Table 3. ^{1}H and ^{13}C NMR spectra of aryl(thienyl)styryl sulfides **IVa**–**IVc** (*E* and *Z* isomers), δ, ppm (*J*, Hz)

Comp. no.	Ph*CH*=	ArS*CH*=	^{3}J	H (Ph)	Thiophene ring		
					H^3	H^4	H^5
IVa (*Z*)	6.47 d (1H)	6.72 d (1H)	15.0	7.06 m (10H)	–	–	–
IVb (*Z*)[a]	7.03 d (1H)	7.24 d (1H)	15.4	7.65 m (9H)	–	–	–
IVb (*E*)[b]	6.82 d (1H)	6.88 d (1H)	11.0	7.65 m (9H)	–	–	–
IVc (*Z*)	6.71 d (1H)	6.97 d (1H)	15.3	7.40 d (H_o, *J* 7.2), 7.44 t (H_m,	7.41 d (1H, $J_{4,3}$	7.17 d. d (1H,	7.51 d (1H)
IVc (*E*)	6.58 d (1H)	6.64 d (1H)	10.9	7.72 d (H_o, *J* 7.2), 7.57 t (H_m,	7.37 d (1H, $J_{4,3}$	7.12 d. d (1H,	7.45 d (1H)

Comp. no.	Ph*C*H=	S*C*H=	C(Ph)	C(SAr)
IVa (*Z*)	129.79	121.23	125–128.5 ($C_{o,m,p}$), 134.34 (C_i)	133.44 (C_i)
IVb (*Z*)[a]	130.56	129.95	126.98 (C_o), 128.26 (C_m), 126.48 (C_p), 137.23 (C_i)	129.76 (C_i), 128.73 (C_o), 128.61 (C_m)
IVb (*E*)[b]	130.44	129.91	126.96 (C_o), 127.32 (C_m), 125.89 (C_p), 137.12 (C_i)	129.63 (C_i), 128.73 (C_o), 128.61 (C_m)
IVc (*Z*)	125.78	128.43	125.66 (C_o), 128.33 (C_m), 127.09 (C_p), 135.93 (C_i)	133.69 (C^3), 127.57 (C4), 129.9 (C^5)
IVc (*E*)	125.65	128.61	128.43 (C_o), 128.10 (C_m), 126.92 (C_p), 135.93 (C_i)	132.78 (C^3), 127.41 (C4), 129.3 (C^5)

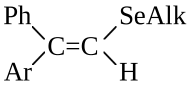
[a] 2.66 t (3H, CH_3). [b] 2.66 t (3H, CH_3).

constants [*J*(SeC=CH) 10.3–10.6 Hz and *J*(SeC=CH) 6.4 Hz] (Table 2). It is known [3] that, depending on the relative position of the olefin proton and selenium, the Se–H coupling constant varies in the following ranges, Hz: $^{2}J_{gem}$ 11–26, $^{3}J_{cis}$ 6–10, and $^{3}J_{trans}$ 1–4. The observed Se–H coupling constants point to mixtures either of *trans*-**I**' and *trans*-**II** isomers or *trans*-**II** and *gem*-**I** isomers.



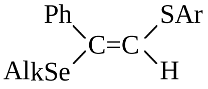
J 6–10 Hz

I



J 11–26 Hz

I'



J 6–10 Hz

II

However, the presence in the ^{13}C NMR spectrum of satellite signals of the CH= group, $^{2}J(^{77}Se–^{13}C)$ 14.6 and 22.2 Hz (Table 2), provides unambiguous evidence against structure **I**' whose $^{1}J(^{77}Se–^{13}C=)$ is ~100 Hz [3]. Regretfully, we failed to determine $^{1}J(^{77}Se–^{13}C=)$ for isomers **Ia**–**Ic** and **IIa**–**IIc**, since the satellite signals from the weakest quaternary carbon signals are obscured by strong benzene carbon signals. The signals were assigned based on the chemical shifts of the CH= proton, calculated by the additive scheme, and by the chemical shifts of olefin carbons.

Thus, the ^{1}H and ^{13}C NMR data provide evidence showing that reaction (1) gives rise to isomers **Ia**–**Ic** and **IIa**–**IIc**. Therewith, isomers **Ia**–**Ic** are formed by geminal addition and isomers **IIa**–**IIc** by *trans* addition of one sulfanyl and one selanyl group by the phenylacetylene triple bond. In both cases, the olefin proton is *cis* to selenium.

The liquid-phase thermal reactions of phenylacetylene with the system arene(hetarene)thio–diselenide studied open the way to the synthesis of previously unknown compounds, 2-alkylselanyl-2-arylsulfanyl-1-phenylethenes and 1-alkylselanyl-2-arylsulfanyl-1-phenylethenes, via conjugate addition to the phenylacetylene triple bond of alkylselanyl and sulfanyl radicals. Such compounds are valuable synthons for introduction of vinyl sulfide fragments in organic molecules.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recoreded on a Bruker DPX-400 spectrometer (90 μHz), internal reference HMDS.

Reaction progress was followed and product analysis was performed by GLC on an LKhM-8-MD-2 chromatograph with linear temperature programming (12 deg/min). Stainless-steel column (1000.3 mm), packing 5% ŒE-60 on Chromaton N-AW-HMDS. Carrier gas helium.

The mass spectra of reaction mixtures and products were obtained on an LKB-2091 GC–MS system, capillary column SB-5 (25 m), ionizing energy 57 eV.

Reaction of phenyl acetylene with the system arene(hetarene)thiol–dialkyl diselenide. A mixture of arenethiol and dialkyl diselenide was added to a stirred and heated (110–140°C) phenylacetylene. Reaction progress was followed by GLC. The resulting products were isolated by vacuum distillation of the reaction mixtures. The reaction conditions and products yields are given in Table 1. The characteristics of compounds **Ia**–**Ic** and **IIa**–**IIc** are given in Table 2.

Reaction of phenylacetylene with arenethiols. Equimolar mixture of phenylacetylene and thiol was left to stand at room temperature or, if required, under heating with stirring. The resulting aryl(thienyl) styryl sulfides **IV** were distilled in a vacuum. The products are light yellow oils. Tables 1 and 2 list the yields and spectral characteristics of compounds **IV**, respectively.

REFERENCES

1. Shilkina, T.A., Papernaya, L.K., Deryagina, E.N., and Albanov, A.I., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 7, p. 1339.
2. Deryagina, E.N., Papernaya, L.K., Shilkina, T.A., and Vvedinskii, V.Yu., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 3, p. 471.
3. Johannsen, I., Henriksen, L., and Eggert, H., *J. Org. Chem.*, 1986, vol. 51, no. 10, p. 1657.