Selenium Heterocycles XII (1). Heat Induced Transformation
of 1,2,3-Selenadiazoles to Disubstituted Selenophenes (2).

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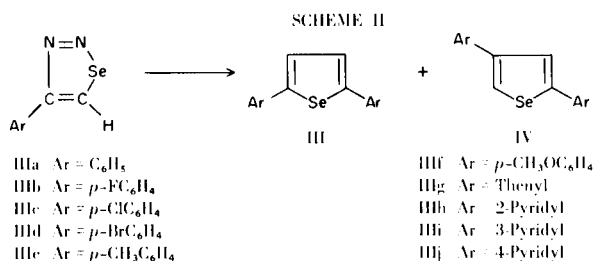
4-Aryl-1,2,3-selenadiazoles when subjected to heat afforded 2,5-diarylselenophenes and small quantities of 2,4-diarylseneophenes. Monoarylacetylenes and selenium behaved similarly. Phenylacetylene and sulfur gave 2,4-diphenylthiophene. Mechanistic aspects of these reactions are discussed.

The synthesis and utility of 1,2,3-selenadiazoles for the preparation of acetylenic compounds by their pyrolysis under reduced pressure have been reported in preceding papers (3-6).
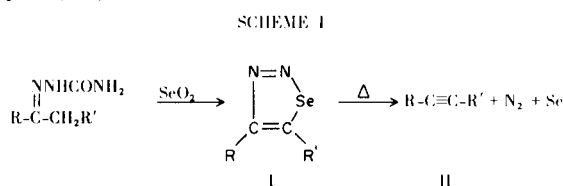
SCHEME I

We now report that the prolonged heating of the decomposition product of I (R = aryl or heterocyclic group, R' = H) affords high yield of 2,5-diarylselenophenes (III) (Scheme II). In the case of 4-phenyl-1,2,3-selenadiazoles the reaction when carried out at 140° gave only 2,5-diphenylselenophene, while at higher temperatures (240-250°) 2,5-diphenylselenophene was separated as the major product along with small quantities of 2,4-diphenyl-selenophene.

SCHEME II

IIIa Ar = C₆H₅   IIIf Ar = p-CH₃OC₆H₄
IIIb Ar = p-FC₆H₄   IIIg Ar = Thenyl
IIIc Ar = p-ClC₆H₄   IIIh Ar = 2-Pyridyl
IIId Ar = p-BrC₆H₄   IIIi Ar = 3-Pyridyl
IIIe Ar = p-CH₃C₆H₄   IIIj Ar = 4-Pyridyl

1,2,3-Selenadiazoles substituted in the 5-position failed to give selenophenes under the reaction conditions.

Two independent routes may be suggested for this ring transformation reaction. In the first a biradical intermediate would lead to the formation of 2,5-disubstituted

diselenine which in turn would lose one selenium atom upon heating to give the appropriate selenophene.

Such a ring contraction process has been observed and reported in dicycloalkadiselenine (6). However, we have observed that 2,5-diphenyldiselenine, prepared by reacting phenylacetylene, selenium and sodium ethoxide in re-fluxing dioxane (7), was quite stable under the conditions used for pyrolysis of 1,2,3-selenadiazoles. Such a biradical mechanism is therefore not operative (Scheme III).

SCHEME III
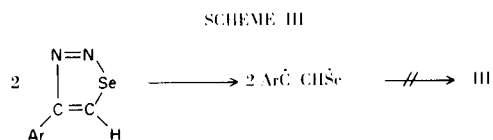
The second route which may be suggested is a two step process: 1,2,3-selenadiazole is first decomposed to the monoarylsubstituted acetylene and selenium. In the second step, monoarylsubstituted acetylenes and selenium interact and afford the corresponding selenophenes. A model study proves that the reaction between selenium and monoarylacetylene under the reaction conditions, give identical results.

It is interesting to note that potassium 2-phenyl-acetylene selenolate (8) when subjected to heat, a mixture of 2,4- and 2,5-diphenylselenophene is obtained. It was suggested, that the hydrogen necessary in this reaction was obtained from decomposition of part of the starting material (Scheme IV).
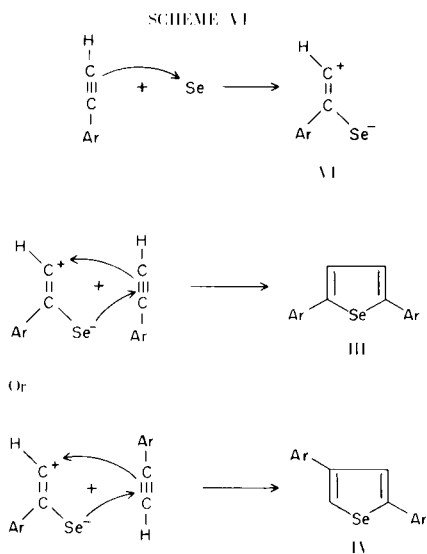
SCHEME IV
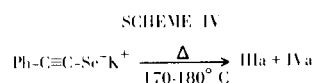
To compare the element of sulfur with selenium, a similar experiment was conducted with phenylacetylene and sulfur. The reaction was vigorous and at 140° hydrogen sulfide was evolved during the course of the reaction. Repetition of this experiment at 100° did not result in the evolution of hydrogen sulfide. In both cases only one isomer (i.e. 2,4-diphenylthiophene) was separated.

SCHEME V
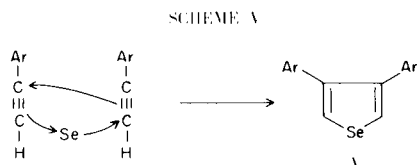
Two different mechanisms are suggested for the formation of 2,4- and 2,5-diarylselenophenes. Careful examination of the reaction product showed that 3,4-diarylselenophene (and thiophene) were not formed even in trace amounts. Therefore a concerted mechanism which on the basis of steric hindrance of aryl groups, predicts the formation of 3,4-isomers (V), was ruled out (Scheme V).

However, an ionic mechanism as illustrated in the Scheme VI seems to be possible:

SCHEME VI

Or

The second possible mechanism involves a biradical species according to the Scheme VII.

Nonformation of 3,4-diphenylseleno and thiophenes supports both mechanisms. This specially refers to species (VI) and (VII) which predict the formation of (III) and (IV).

All compounds prepared are tabulated in Table I.

TABLE I

Compound	Ar	Yield %	M.p. °C	Cryst. Solvent	UV$_{max}$ (nm)	Formula	C% Calcd.	C% Found	H% Calcd.	H% Found
IIIa	C_6H_5	65	170-172 (a)	Ethanol + Water	326	$C_{16}H_{12}Se$	67.84	67.49	4.23	4.30
IIIb	p-FC_6H_4	35	188-191	Ethanol + Water	323	$C_{16}H_{10}F_2Se$	60.18	60.06	3.13	3.12
IIIc	p-ClC_6H_4	38	185-188	Acetone + Water	331	$C_{16}H_{10}Cl_2Se$	54.57	54.38	2.83	2.90
IIId	p-BrC_6H_4	48	214-216	Acetone	338	$C_{16}H_{10}Br_2Se$	43.57	43.55	2.26	2.27
IIIe	p-$CH_3C_6H_4$	69	192-194	Acetone + Water	323	$C_{18}H_{16}Se$	69.45	69.36	5.13	5.21
IIIf	p-$CH_3OC_6H_4$	40	219-222	2-Ethoxyethanol	333	$C_{18}H_{16}O_2Se$	62.98	62.71	4.65	4.56
IIIg	2-Thenyl	60	131-133	Acetone + Water	333	$C_{12}H_8S_2Se$	48.81	48.97	2.71	2.73
IIIh	2-Pyridyl	70	173-175	Ethanol + Water	306	$C_{14}H_{10}N_2Se$	58.96	58.80	3.50	3.44
IIIi	3-Pyridyl	32	104-106	Benzene + Pet. Ether	304	$C_{14}H_{10}N_2Se$	58.96	58.91	3.50	3.51
IIIj	4-Pyridyl	28	123-126	Benzene + Pet. Ether	301	$C_{14}H_{10}N_2Se$	58.96	58.81	3.50	3.43

(a) Lit. (9), 171°.

SCHEME VII

VII

III

IV
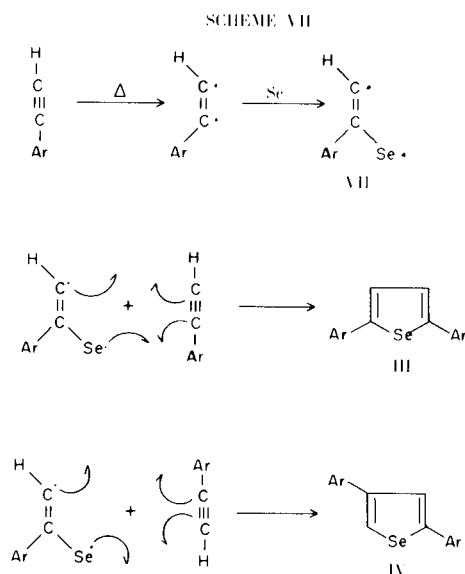
EXPERIMENTAL

Melting points were determined on a Kofler hot stage microscope and are uncorrected. Nmr spectra were determined using Varian A60A and T-60 spectrometers. Mass spectra were run on a Varian model MAT CH5. Uv spectra were determined on a Varian Techtron 653 spectrometer.

2,5-Di-p-tolylselenophene (IIIe).

4-p-Tolyl-1,2,3-selenadiazole (3) 1.12 g. (5 mmoles) was decomposed portionwise in a small round bottom flask, maintained in an oil bath at 180°. After the vigorous decomposition subsided, the temperature of the bath was raised to 245-250° and maintained at this temperature for 30 minutes. The reaction mixture was first subjected to vacuum sublimation or directly recrystallized from an acetone-water mixture (70:30) to give 0.54 g. (60%) of (IIIe) m.p. 192-194°; molecular weight by mass spectroscopy m/e 312; uv max 232 nm; nmr (deuterochloroform): δ 2.43 (s, 6H, CH₃), 7.43 (s, 2H, CH), 7.43 (m, 8H, phenyl), ppm. Concentration of the mother liquor gave a residue, which was recrystallized three times from ethanol to give 0.08 g. (10%) of 2,4-di-p-tolylselenophene, m.p. 140°; uv max 267 nm [lit. (10) m.p. 140°, uv max 267 nm]. All other 2,5-diarylselenophenes were prepared similarly.

Reaction of Phenylacetylene and Selenium.

Powdered black selenium (3.16 g., 0.04 mole) and 8.16 g. (0.08 mole) of freshly distilled phenylacetylene was heated at 140° for 4 hours. The reaction mixture was dissolved in chloroform and chromatographed on a short column containing silica gel with layers fo active charcoal. After evaporation of the solvent,

the residue was recrystallized from ethanol to give 3.4 g. (30%) of yellowish flakes. Further recrystallization from ethanol gave silver shining flakes m.p. 172°; molecular weight by mass spectroscopy m/e 283; uv max 326 nm. The compound was found to be identical with 2,5-diphenylselenophene (IIIa).

Reaction of Phenylacetylene and Sulfur.

Powdered sulfur (0.64 g., 0.02 mole) and 4.08 g. (0.04 mole) of freshly distilled phenylacetylene was heated gently. A vigorous reaction started and hydrogen sulfide was evolved. After heating for 20 minutes, the reaction mixture was worked up as above. A yellowish crystalline compound 1.5 g. (32%) was obtained and identified to be 2,4-diphenylthiophene; m.p. 120°; molecular weight by mass spectroscopy m/e 236; uv max 258 nm.

Pyrolysis of Potassium 2-Phenylacetylene Selenolate.

A mixture of (0.5 g., 23 mmoles) potassium 2-phenylacetylene selenolate (7), and 1 g. of dry sand was heated on a metalic bath to 170° in a microdistillation apparatus. A yellow liquid was distilled (85 mg.), which was solidifed (m.p. 102-123°). After recrystallization from alcohol, yellowish plates were obtained m.p. 172°. The compound was identical with 2,5-diphenylselenophene (IIIa). Uv examination of the crude product revealed that 2,4-isomer was also present in a small amount. Two maxima were observed, one with λ max 326 nm corresponding to the 2,5-isomer and the other with λ max 262 nm corresponding to the 2,4-isomer (IVa) [lit. (10) 262 nm].

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