THERMAL TRANSFORMATIONS OF ALLYL 2-THIENYL SULFIDE AND SELENIDE

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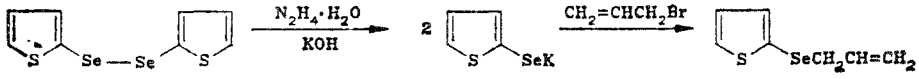
In the gas phase at 350-410°C allyl 2-thienyl sulfide is converted to thiophene-2-thiol, di(2-thienyl) sulfide, and 2-methylthieno[2,3-b]thiophene. In the presence of acetylene thieno[2,3-b]thiophene is formed in addition to these products. Allyl 2-thienyl selenide is converted quantitatively to 2,3-dihydro-2-methylselenopheno[2,3-b]thiophene during fractional distillation in vacuo. Thiophene, di(2-thienyl) selenide, di(2-thienyl) diselenide, thiophene-2-selenol, and 2-methylselenopheno[2,3-b]thiophene are formed in addition to these compounds in the thermolysis of allyl thienyl selenide in the gas phase. In the presence of acetylene the thermal decomposition of allyl thienyl selenide is accompanied by the formation of selenophene.

When they are heated (for example, in refluxing quinoline), allyl aryl and allyl thienyl sulfides undergo the thio-Claisen rearrangement, the product (I) of which undergoes intramolecular cyclization to give 2,3-dihydrothiophene and thiopyran derivatives [1, 2].

In the thermolysis of allyl thienyl sulfides intermediates I were isolated either in the form of S-benzoyl derivatives [2] or directly [3].

We have studied the thermolysis of allyl 2-thienyl sulfide (II) and selenide (III), as well as their cothermolysis with acetylene (which, as is known [4, 5], is a trap for phenylthiyl and thienylthiyl radicals), in the gas phase.

Sulfide II was synthesized via a previously described method [2], while selenide III was obtained for the first time by a modified method [6] via the following scheme:



III

It is known [2, 3] that sulfide II is quite stable. It undergoes fractional distillation in vacuo without any changes and, in the absence of light, can be stored for a long time in a refrigerator. In the case of thermolysis in the gas phase in a nitrogen atmosphere its complete conversion is observed at and above 380°C. At 350-410°C the principal thermolysis products are thiophene-2-thiol (IV), di(2-thienyl) sulfide (V), and 2-methylthieno[2,3-b]thiophene (VI).

Compounds IV and V are evidently formed through thermal transformations of thienylthiyl radicals (VII) (via the schemes presented in [7]). Radical VII is the primary product of the thermal decomposition of sulfide II. 2-Methylthienothiophene VI is most likely formed through a thio-Claisen rearrangement of sulfide II. The intermediate product of intramolecular cyclization of thiol VIII — 2-methyl-2,3-dihydrothieno[2,3-b]thiophene — was not detected over the investigated temperature range.

The reaction of allyl thienyl sulfide II with acetylene at 370-460°C (see Table 1) gives, in addition to IV-VI, thieno[2,3-b]thiophene (IX). Its formation is due to the addition of thienylthiyl radicals (VII) to acetylene (see [5]). (See scheme in the middle the next page.)

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TABLE 1. Yields of the Products of the Gas-Phase Reaction of Allyl Thienyl Sulfide II with Acetylene (1:4)

Expt.	T, °C	Conversion of sulfide	Yields of the reaction products, % (acc. GLC)*				
			Thiophene	IV	V	VI	IX
1	370	54	Traces	27	13	26	14
2	410	83	Traces	28	15	18	21
3	430	92	3	37	11	11	20
4	460	96	5	14	17	10	25

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*Based on the unchanged sulfide II.

TABLE 2. Mass Spectra of Selenium-Containing Thiophene Derivatives III and XI-XIII

Compound	m/z* (I_{rel}, %)
III	204 (70) $[M^+]$; 163 (100) $[M-C_3H_5]^+$; 83 (20) $[M-C_3H_5Se]^+$
XI	204 (100) $[M^+]$; 189 (30) $[M-CH_3]^+$; 175 (10) $[M-C_2H_5]^+$; 124 (16) $[M-Se]^+$; 123 (20) $[M-SeH]^+$
XII	244 (24) $[M^+]$; 203 (90) $[M-C_3H_5]^+$; 162 (2) $[M-2C_3H_5]^+$; 122 (8) $[M-C_3H_5-SeH]^+$; 121 (100) $[M-C_3H_5-H_2Se]^+$; 83 (4) $[C_4H_3S^+]$
XIII	284 (20) $[M^+]$; 243 (30) $[M-C_3H_5]^+$; 202 (80) $[M-2C_3H_5]^+$; 121 (100) $[M-2C_3H_5-SeH]^+$; 83 (5) $[C_4H_3S]^+$

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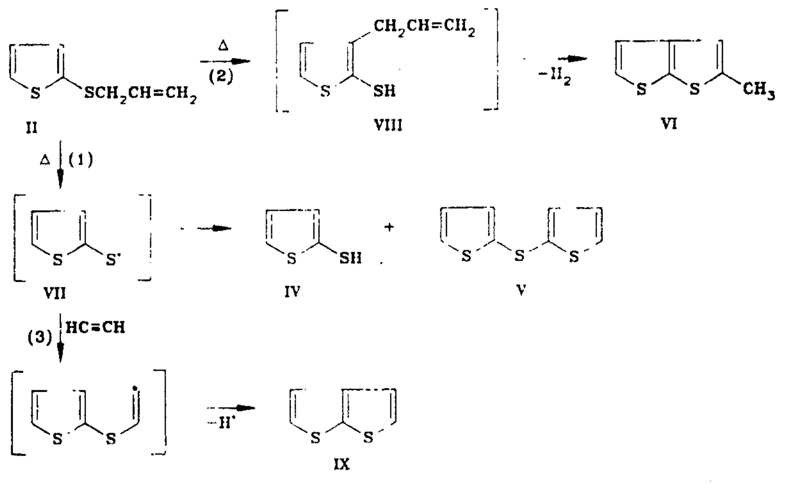
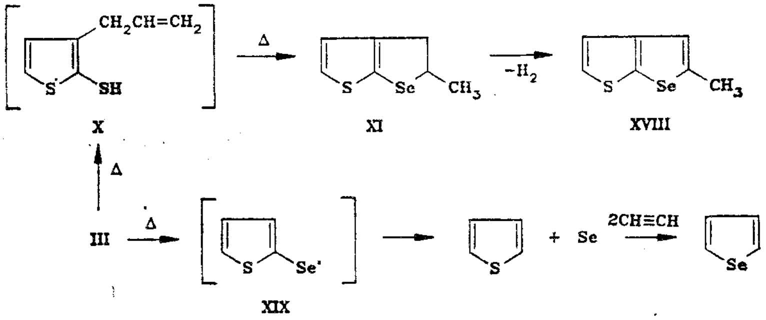
*The m/z values of the selenium-containing ions are presented only for the ^{80}Se isotope.



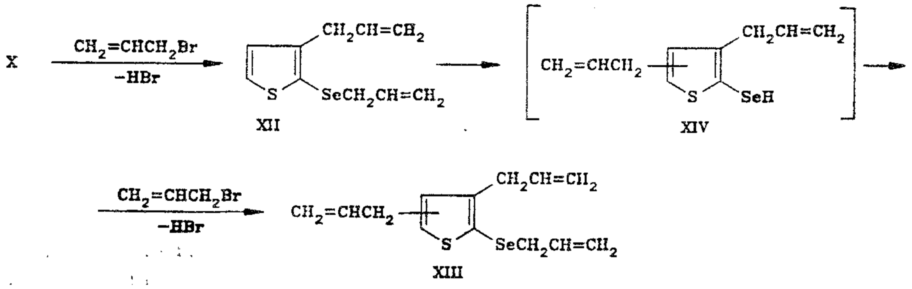
Thus the thermal transformations of sulfide II in the gas phase take place simultaneously via schemes (1) and (2); thiyl radicals VII, which are readily generated via scheme (1), are converted either to thiol IV and sulfide V or (in the presence of acetylene) react via scheme (3). The transformation via scheme (3) dominates at higher temperatures. However, above 460°C the reaction of allyl thienyl sulfide II with acetylene is accompanied by substantial resinification.

In contrast to sulfide II, selenide III cyclizes extremely readily, undergoing beforehand a seleno-Claisen rearrangement. Selenide III is converted in part to XI even during its synthesis. Upon subsequent vacuum fractionation the reaction goes to completion, and XI is isolated in virtually quantitative yield. This reaction can be recommended as a preparative method for the synthesis of 2-methyl-2,3-dihydroselenopheno[2,3-b]thiophene (XI). Intermediate X was not detected either in the synthesis of selenide II or during isolation of cyclic product XI.

However, two substances, to which, judging from the set of molecular-ion peaks and the character of the fragmentation (see Table 2), structures XII and XIII (see [3]) can be assigned, were identified by chromatographic mass-spectrometric methods in the product that was isolated directly during synthesis and not subjected to fractional distillation.



Compounds XII and XIII are evidently formed by alkylation by allyl bromide of intermediates X and XIV — the primary products of seleno-Claisen rearrangement of selenides III and XII.



According to the GLC data, the yield of selenide XII is 3-4%, while the yield of XIII does not exceed 1-2%.

In the gas phase in a stream of nitrogen at 320°C selenide III is primarily converted to cyclic compound XI (in ≈70% yield). Di(2-thienyl) selenide (XV, 7% yield), di(2-thienyl) diselenide (XVI, 5% yield), thiophene-2-selenol (XVII, 3% yield), and thiophene (6% yield) are formed in addition to it. In addition, 2-methylselenopheno[2,3-b]thiophene (XVII), which is formed by dehydrogenation of dihydro derivative XI, was detected in the reaction products, and the walls of the reactor were coated appreciably with elementary selenium.

The XVIII:XI ratio increases with an increase in the temperature; at 440°C selenide XI is virtually absent, while methylselenophenothiophene XVIII is formed in 28% yield. The principal reaction product in this case is thiophene (in ≈50% yield).

The character of the reaction products formed changes slightly in the thermolysis of selenide III in the presence of acetylene at 400-440°C; selenophene, which is evidently a product of the known thermal reaction of selenium with acetylene [8], is also formed in addition to XV-XVII. The yield of selenophene increases with an increase in the temperature and reaches 20% at 440°C. The 2-thienylselenyl radical (XIX) generated from selenide III is evidently unstable and readily decomposes with the liberation of elementary selenium. Evidence for the thermal stability of radical XIX is also provided by absence of a product of its reaction with acetylene.

Thus, in contrast to allyl phenyl sulfide and selenide, a Claisen rearrangement, to which selenide III is inclined to a greater degree, occurs in addition to thermal decomposition in the thermolysis of II and III in the gas phase.

EXPERIMENTAL

The NMR spectra were recorded with a Tesla BS 567A spectrometer (100 MHz) with hexamethyldisiloxane (HMDS) as the internal standard; the chemical shifts are presented on the δ scale (in parts per million). The mass spectra were obtained with an MAT-212 chromatographic mass spectrometer at an ionizing voltage of 70 eV using a Varian-3700 chromatograph with SE-54 as the liquid phase.

Analysis by GLC was accomplished with an LKhM-8MD-5 chromatograph with XE-60 as the liquid phase on Chezasorb under linear-programming conditions (12°C/min) of the column (3 by 2000 mm) temperature with helium as the carrier gas.

The results of elementary analysis of XI for C, H, S, and Se were in agreement with the calculated values.

Allyl 2-Thienyl Selenide (III). A 19.5-g (0.06 mole) sample of di(2-thienyl) diselenide [9] was added at 80-90°C to a solution of 6.7 g (0.12 mole) of KOH in 30 ml of hydrazine hydrate, after which the mixture was cooled, and 11 ml (0.12 mole) of allyl bromide was added dropwise. The organic layer was separated, washed with water, and dried with $CaCl_2$. According to GLC data, it contained 88% selenide III, 3% diallyl selenide, 4% cyclization product XI, 3% allyl 3-allyl-2-thienyl selenide (XII), and ≈ 1% allyl diallyl-2-thienyl selenide XIII. The yield of selenide III was 86%. PMR spectrum ($CDCl_3$): 3.37 (d, $Se-CH_2$), 4.94 (m, $=CH_2$), 5.88 (m, $-CH=$), 6.95 (dd, thiophene 4-H), 7.14 (dd, 3-H), 7.35 ppm (dd, 5-H).

Compounds XII and XIII were identified by chromatographic mass spectrometry (see Table 2).

2,3-Dihydro-2-methylselenopheno[2,3-b]thiophene (XI, C_7H_8SSe). The vacuum fractionation of selenide III gave a fraction with bp 107-110°C (4 mm), which was identified as pure XI with n_D^{20} 1.6550. PMR spectrum ($CDCl_3$): 1.61 (d, CH_3), 2.69 (dd), 3.14 (dd, CH_2), 4.58 (m, $-CH-$), 6.72 (d, thiophene 4-H), 7.04 ppm (d, 5-H); $^3J_{CH-CH_3} = 7.0$, $^2J_{CH_2} = 15.0$, $^3J_{CH-CH_2} = 7.0$, $^3J_{45} = 5.2$ Hz. ^{13}C NMR spectrum ($CDCl_3$): 23.14 (CH_3), 40.91 (CH_2), 49.66 (CH), 123.64 [$C_{(4)}$], 127.27 [$C_{(5)}$], 130.78 [$C_{(3)}$], 144.22 ppm [$C_{(2)}$]; $^1J_{Se-C(H)} = 44.0$ Hz.

The thermolysis of II and III in a stream of nitrogen and their thermal reaction with acetylene were realized in a tubular quartz reactor with a diameter of 15 mm in the annular gap formed by the walls of the reaction tube and the housing of the thermocouple; the length of the reaction zone was 250 mm. Chalogenides II and III were introduced into the reaction zone by spraying with an automatic dispenser at a rate of 3.2 ml/h. The nitrogen feed-in rate was 1 liter/h, and the acetylene feed-in rate corresponded to a reagent ratio of 1:4. The reaction products were condensed in cooled traps and were subjected to analysis by GLC and chromatographic mass spectrometry. The yields of the products were calculated from the GLC data.

Thiophene-2-thiol (IV), di(2-thienyl) sulfide (V), thiophene, selenophene, di(2-thienyl) selenide (XVI), and thiophene-2-selenol (XVII) were identified by GLC (by comparison with genuine samples) and chromatographic mass spectrometry.

2-Methylthieno[2,3-b]thiophene (VI). In the vacuum fractionation of the condensates obtained in the thermolysis of sulfide II the fraction with bp 100-115°C (10 mm) contained ≈85% VI. It was isolated in pure form by preparative GLC with a PAKhV-07 chromatograph with a stainless-steel column (10 by 5000 mm) packed with Lucoprene G-1000 on Chromaton N-AW-DMCS; the separation temperature was 120°C. PMR spectrum (d_6-acetone): 2.50 (broad s, CH_3), 6.93 (3-H), 7.13 (4-H), 7.39 ppm (5-H); according to the data in [10], the spectrum contained the following peaks, respectively: 2.48, 6.94, 7.14, 7.39 ppm; $J_{CH_3-3-H} = 1.2$ Hz.

Thieno[2,3-b]thiophene (IX). This compound was liberated in the vacuum fractionation of the condensates obtained in the cothermolysis of sulfide II with acetylene [bp 100-120°C (15 mm)] and was purified by preparative GLC under the conditions used to isolate VI (see above). PMR spectrum (d_6-acetone): 7.23 (d, 3-H, 4-H), 7.44 ppm (d, 2-H, 5-H) (see [11]).

2-Methylselenopheno[2,3-b]thiophene (XVIII). This compound was liberated in the vacuum fractionation of the condensates obtained in the thermolysis of selenide III at 430°C and had bp 150-152°C (23 mm). PMR spectrum ($CDCl_3$): 2.61 (broad s, CH_3), 7.30 ppm (m). Mass spectrum: M^+ 202, M_{calc} 202 (for ^{80}Se).

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