ALKYNYL DERIVATIVES OF SELENOPHENE

II.* ADDITION OF THIOLS TO SELENIENYL ALKYNYL KETONES

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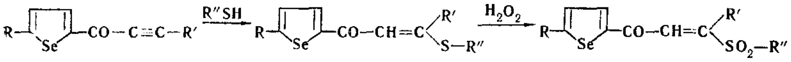
The reaction of selenienyl alkynyl ketones with thiophenol and butyl mercaptan gave good yields of selenienylketovinyl sulfides. The corresponding sulfones were obtained from some of the sulfides by oxidation with hydrogen peroxide. The IR spectra of the synthesized compounds are discussed.

We have previously [1] developed a method for the preparation of ketovinyl sulfides of the thiophene series and have proved that the addition of a nucleophilic reagent (thiophenol) to thienyl alkynyl ketones occurs at the β position relative to the carbonyl group. In the present study, in a search for biologically active compounds we obtained ketovinyl sulfides of the selenophene series by the addition of thiophenol and butyl mercaptan to selenienyl alkynyl ketones.



I–VII VIII, IX

I R=H, R′=C_4H_9, R″=C_6H_5; II R=H, R′=R″=C_6H_5; III R=Br, R′=R″=C_6H_5; IV R=CH_3, R′=R″=C_6H_5; V R=H, R′=C_6H_5, R″=C_4H_9; VI R=Br, R′=C_6H_5, R″=C_4H_9; VII R=CH_3, R′=C_6H_5, R″=C_4H_9; VIII R=Br, R′=R″=C_6H_5; IX R=H, R′=C_6H_5, R″=C_4H_9

The addition of thiophenol to selenienyl alkynyl ketones, which was carried out at room temperature in the presence of a basic catalyst (triethylamine), proceeds smoothly and gives high yields of the corresponding vinyl ketones (I-IV). Increasing the reaction time results in pronounced resinification and a reduction in the yields of the reaction products. The addition of butyl mercaptan to the selenienyl alkynyl ketones was accomplished at 70°C.

It must be noted that substituents in the 5 position of the selenophene ring have an appreciable effect on the reaction of selenienyl alkynyl ketones with thiols. An electron-donor substituent (CH_3) lowers the electrophilicity of the triple bond and hinders the addition of thiols – the yields of IV and VII were 41% and 23%, respectively. The introduction of a bromine atom into the selenophene ring raises the reaction product yields considerably – the yields of III and VI were 92% and 67%, respectively.

The synthesized selenienylketovinyl sulfides (I-VII) are brightly colored crystals (see Table 1) that are quite soluble in benzene, alcohol, and ether.

Compounds III and V were oxidized with hydrogen peroxide in glacial acetic acid to the corresponding sulfones (VIII and IX).

The IR spectra of I-VII contain absorption bands of the selenophene ring at 1425-1436, 1335-1340, and 1230-1245 cm^{-1}, and the band at 680-685 cm^{-1} corresponds to the stretching vibrations of the C–S bond. The absorption bands of the carbonyl group and the double bond are found, respectively, at 1604-1612 and

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*See [1] for communication I.

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TABLE 1. Ketovinyl Sulfides and Sulfones of the Selenophene Series

Compound	Appearance	mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
				C	H	S	Se	C	H	S	Se	
I	Bright-yellow plates	74	$C_{17}H_{18}OSSe$	58,30	5,16	9,11	22,81	58,45	5,12	9,16	22,63	65
II	Brown needles	189—191	$C_{19}H_{14}OSSe$	61,66	3,81	8,67	21,86	61,78	3,79	8,66	21,40	86
III	Dark-yellow plates	155—157	$C_{19}H_{13}BrOSSe$[a]	—	—	7,28	—	—	—	7,14	—	92
IV	Light-orange plates	144—146	$C_{20}H_{16}OSSe$	62,78	4,11	8,45	21,08	62,66	4,17	8,34	20,62	41
V	Bright-yellow needles	85	$C_{17}H_{18}OSSe$	58,42	5,14	9,65	22,28	58,45	5,12	9,16	22,63	55
VI	Bright-yellow needles	86—88	$C_{17}H_{17}BrOSSe$[b]	—	—	7,48	—	—	—	7,42	—	67
VII	Yellow needles	47	$C_{18}H_{20}OSSe$	60,02	5,58	8,76	21,28	59,50	5,50	8,81	21,76	23
VIII	Yellow oil	—	$C_{17}H_{18}O_3SSe$	53,81	4,80	8,62	20,66	53,54	4,72	8,40	20,73	65
IX	Yellow oil	—	$C_{19}H_{13}BrO_3SSe$[c]	—	—	6,81	—	—	—	6,67	—	60

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a) Found: Br 17.92%. Calculated: Br 17.86%.

b) Found: Br 18.45%. Calculated: Br 18.56%.

B) Found: Br 16.78%. Calculated: Br 16.67%.

1535-1540 cm^{-1}. If $\nu_{C=O}$ and $\nu_{C=C}$ of I-VII and of ketovinyl sulfides of similar structure of the thiophene series [1] are compared, the frequency of the stretching vibrations of the carbonyl group of the selenophene derivatives is, as a rule, 20-40 cm^{-1} lower, while the values for the double bond are generally 40-50 cm^{-1} lower for the selenophene derivatives. It is known that intensification of the donor properties of groups leads to a decrease in the vibrational frequency of the C=O bond [2]. The selenophene group consequently has a stronger electron-donor effect than the thiophene group in compounds of similar structure, which is in agreement with the results in [3, 4].

EXPERIMENTAL

3-Phenylthio-1-(2-selenienyl)-2-hepten-1-one (I). A solution of 0.22 g (0.002 mole) of thiophenol in 15 ml of ethanol was added slowly dropwise to a solution of 0.5 g (0.002 mole) of 1-(2-selenienyl)-2-heptyn-2-one in 20 ml of ethanol containing 0.05 g (0.5 mmole) of triethylamine. The reaction mixture was stirred at room temperature for 2 h, the solvent was evaporated, and the precipitated crystals were removed by filtration and recrystallized from ethanol to give 0.62 g (65%) of bright-yellow plates with mp 74°.

Compounds II-IV were similarly obtained.

3-Phenyl-3-butylthio-1-(2-selenienyl)-2-propen-1-one (V). A solution of 0.63 g (0.007 mole) of butyl mercaptan in 20 ml of ethanol was added slowly dropwise at room temperature with stirring to a solution of 2 g (0.007 mole) of 3-phenyl-1-(2-selenienyl)-2-propyn-1-one containing 0.2 g (0.002 mole) of triethylamine. The mixture was refluxed and stirred for another hour. The solvent was evaporated, and the precipitated crystals were removed by filtration to give 1.5 g (55%) of bright-yellow needles with mp 85-86° (from ethanol).

Compounds VI and VII were similarly obtained.

3-Phenyl-3-butylsulfonyl-1-(2-selenienyl)-2-propen-1-one (IX). A total of 1 ml of 30% hydrogen peroxide was added slowly to a cooled (to 0°) solution of 1.4 g (0.004 mole) of V in 20 ml of glacial acetic acid. The mixture was heated on a water bath for 1.5 h, cooled, and poured into water. The mixture was extracted with ether, and the extract was dried over calcined magnesium sulfate. The solvent was evaporated, and the residue was dried in vacuo to give 0.98 g (65%) of a light-yellow oil.

Compound VIII was similarly obtained.

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