ALKYNYL DERIVATIVES OF SELENOPHENE

I. SYNTHESIS AND SOME TRANSFORMATIONS OF SELENIENYL ALKYNYL ALCOHOLS AND KETONES

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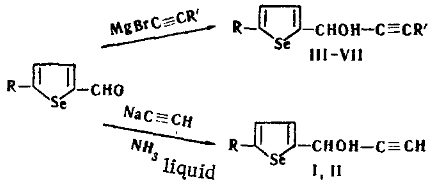
The reaction of alkylacetylenes and acetylenes with 2-formylselenophene and its derivatives has given the previously unknown selenienyl alkynyl alcohols, which are oxidized to the corresponding ketones by MnO_2. The reactions of the latter with hydrazine and hydroxylamine were investigated, as a result of which selenienyl-substituted pyrazoles and isoxazoles were obtained.

A large number of studies [1-5] have been devoted to the synthesis and systematic study of the properties of oxygen-containing alkynyl derivatives of furan and thiophene. In the selenophene series, this class of substances was unknown until now. It seemed of interest to compare the properties of the alkynyl alcohols and ketones of the selenophene series with the analogous compounds of thiophene and furan. In addition, the alkynyl derivatives of selenophene open up possibilities for the synthesis of compounds that are promising in a practical respect.

In this paper we have accomplished the synthesis of alkynyl alcohols of the selenophene series by the reaction of substituted 2-formylselenophenes with alkynylmagnesium bromides under the conditions of the Iotsich reaction and with sodium acetylide in liquid ammonium.

Alcohols I and II (obtained in 80-85% yields) and III and IV (obtained in 65-80% yields) are oily liquids that are stable on storage in air and have higher boiling points than the thiophene analogs [3].



I $R=H$; II $R=CH_3$; III $R=H$, $R'=C_4H_9$;
IV $R=H$, $R'=C_6H_{13}$; V $R=H$, $R'=C_6H_5$;
VI $R=Br$, $R'=C_6H_5$; VII $R=CH_3$, $R'=C_6H_5$

Phenyl-substituted selenienyl alkynyl alcohols V-VII are extremely unstable compounds. Because of this, they were oxidized to the corresponding ketones without prior purification.

The IR spectra of I-IV have broad absorption bands of associated hydroxyl groups at 3400-3430 cm^{-1}, absorption bands of the triple bond at 2220-2240 cm^{-1} (for III and IV) and at 2100 cm^{-1} (for I and II), as well as bands at 1425-1450, 1310-1345, 1215-1230, 835-850, and 718 cm^{-1}, which are characteristic for the selenophene ring. It should be noted that there is an absorption band of a conjugated carbonyl group at 1615-1627 cm^{-1} in the IR spectra of III and IV obtained via the Iotsich reaction. The formation of a small amount of ketone can be explained by the side reaction of the starting 2-formylselenophene with magnesium alkoxide [6].

Selenienyl alkynyl ketones were obtained by oxidation of the corresponding alcohols with active manganese dioxide in ether (Table 1). Alcohols I and II, with labile alkynyl hydrogens, are oxidized to form

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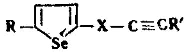
TABLE 1. Selenienyl Alkynyl Alcohols and Ketones



Compound	X	R	R′	bp (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Empirical formula	Found % C	Found % H	Found % Se	Calc. % C	Calc. % H	Calc. % Se	Yield, %
I	CHOH	H	H	115—116 (6)	1,5860	1,5200	41,21	41,96	C_7H_6OSe	45,60	3,51	41,84	45,40	3,28	42,71	85
II	CHOH	CH_3	H	123—125 (4)	1,5860	1,4545	46,19	45,91	C_8H_8OSe	48,29	4,01	39,23	48,24	4,02	39,69	89
III	CHOH	H	C_4H_9	125—126 (2)	1,5770	1,3008	60,93	60,48	$C_{11}H_{14}OSe$	54,81	6,05	32,65	54,77	5,81	32,78	75
IV	CHOH	H	C_6H_{13}	144—146 (1)	1,5482	1,2063	71,19	71,43	$C_{13}H_{18}OSe$	57,91	6,41	29,07	57,99	6,68	29,37	65
VIII	CO	H	C_4H_9	154—156 (2)	1,5861	1,3115	58,97	58,93	$C_{11}H_{12}OSe$	55,20	5,08	33,11	55,23	5,02	33,05	60
IX	CO	H	C_6H_{13}	oil	—	—	—	—	$C_{13}H_{16}OSe$	58,40	6,02	30,12	58,43	5,99	29,59	55
X	CO	H	C_6H_5	*	—	—	—	—	$C_{13}H_{18}OSe$	57,65	6,72	29,25	57,99	6,69	29,37	91
XI	CO	Br	C_6H_5	**	—	—	—	—	$C_{13}H_7BrOSe$	46,20	1,99	23,37	46,15	2,07	23,37	78
XII	CO	CH_3	C_6H_5	***	—	—	—	—	$C_{14}H_{10}OSe$	61,74	3,65	28,99	61,84	3,66	28,94	52

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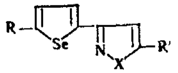
* mp 68-70°.

† mp 96-98°.

‡ mp 47-48°.

TABLE 2. Selenienyl-Substituted Pyrazoles and Isoxazoles



Compound	X	R	R′	mp	Empirical formula	N, % found	N, % calc.	Yield, %
XIII	NH	H	C_4H_9	62—64	$C_{11}H_{14}N_2Se$	11,29	11,06	90
XIV	NH	H	C_6H_{13}	56—58	$C_{13}H_{18}N_2Se$	9,62	9,96	85
XV	NH	H	C_6H_5	179—181	$C_{13}H_{10}N_2Se$	10,28	10,60	78
XVI	NH	CH_3	C_6H_5	200—202	$C_{14}H_{12}N_2Se$	9,69	9,96	72
XVII	NH	Br	C_6H_5	193—195	$C_{13}H_9BrN_2Se$	8,11	7,95	70
XVIII	O	Br	C_6H_5	100—101	$C_{13}H_8BrNOSe$	3,87	3,96	80
XIX	O	CH_3	C_6H_5	70—72	$C_{14}H_{11}NOSe$	5,20	4,89	75
XX	O	H	C_6H_5	83—84	$C_{13}H_9NOSe$	5,13	5,10	85
XXI	O	H	C_4H_9	*	$C_{11}H_{14}NOSe$	5,50	5,48	83

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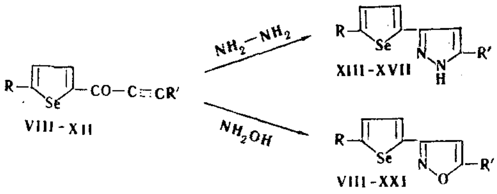
* bp 137-139° (1 mm).

amorphous brown powders that have melting points of about 200°. The molecular weights (determined by the Rast method) indicate that these compounds are dimers.

There is a narrow absorption band of the $C\equiv C$ bond at 2210-2235 cm^{-1} in the IR spectra of selenienyl alkynyl ketones VIII-XII. The absorption band at 1615-1620 cm^{-1} corresponds to a conjugated carbonyl group. The frequency of the $C=O$ vibrations for analogous thiophene compounds lies at 1635-1640 cm^{-1} [3]. The decrease in $\nu_{C=O}$ by 20 cm^{-1} in the spectra VIII-XII as compared with the analogous thienyl alkynyl ketones is explained by the fact that the selenienyl radical has stronger electron-donor character than the thienyl radical, in agreement with the results in [7].



The selenienyl akynyl ketones readily react with hydrazine and hydroxylamine in aqueous ethanol by undergoing intramolecular cyclization to form the corresponding selenienyl-substituted pyrazoles (XIII-XVII) and isoxazoles (XVIII-XXI) (Table 2).

In addition to the frequencies of the selenophene ring, the IR spectra of XIII-XVII contain an intense absorption consisting of a number of bands at 1405-1580 cm^{-1}. They can be assigned to the vibrations of the $C=C$ and $C=N$ bonds of the pyrazole ring. The broad band at 3430 cm^{-1} is assigned to the vibrations of the three N-H bonds.

The series of bands at 1400-1605 cm^{-1} in the IR spectra of XVIII-XXI corresponds to the vibrations of the $C=C$ and $C=N$ bonds of the isoxazole ring, while the narrow band at 930 cm^{-1} corresponds to vibrations of the $C-O$ bond.

EXPERIMENTAL

1-(2-Selenienyl)-2-propyn-1-ol (I). A solution of 15.9 g (0.1 mole) of 2-formylselenophene in absolute ether was added to sodium acetylide obtained from acetylene and 4.6 g (0.2 g-atom) of Na in 700 ml of liquid ammonia. The contents of the flask were stirred for 2 h and allowed to stand overnight. The reaction mixture was decomposed with dry NH_4Cl, the ammonia was evaporated, and 200 ml of ether was poured into the flask. The insoluble material was separated and washed repeatedly with ether. The ether layer was combined with the ether extracts, washed with 10% $NaHSO_3$ and water, and dried with $MgSO_4$. The solvent was evaporated, and the residue was vacuum distilled to give 15.7 g (85%) of I. Compound II was similarly obtained.

1-(2-Selenienyl)-2-heptyn-1-ol (III). A 4.1 g (0.05 mole) sample of butylacetylene in an equal volume of tetrahydrofuran was added to a Grignard reagent prepared from 1.2 g (0.05 g-atom) of magnesium and 5.46 g (0.05 mole) of ethyl bromide in 70 ml of tetrahydrofuran with cooling to 0°. The mixture was heated on a water bath for 5 h, cooled to 0°, and 8 g (0.05 mole) of 2-formylselenophene was added. The mixture was stirred for another 2 h and allowed to stand overnight. It was decomposed with 10% NH_4Cl. The organic layer was separated, and the aqueous layer was extracted three times with ether. The ether extracts and the organic layer were washed with water until they gave a neutral reaction and were then dried with $MgSO_4$. The solvent was evaporated, and the residue was vacuum distilled to give 9 g (75%) of III. Compounds IV-VII were similarly obtained. Alcohols V-VII were oxidized to the corresponding ketones without prior purification.

1-(2-Selenienyl)-2-heptyn-1-one (VIII). Active manganese dioxide [4.35 g (0.05 mole]) was added in small portions with vigorous stirring to a solution of 2.41 g (0.01 mole) of III in 60 ml of dry benzene. The mixture was stirred for 3 h under nitrogen at the boiling point of the solvent, and the resulting precipitate was filtered and thoroughly washed on the filter with ether. The filtrate was washed with water and dried with Na_2SO_4. The ether was evaporated, and the residue was vacuum distilled to give 1.43 g (60%) of VIII. Compounds IX-XII were similarly obtained. Ketone IX was isolated by chromatography on Al_2O_3 with elution by ether-benzene (1 : 3). Ether was used as the solvent to obtain X-XII, and the reaction time was 2 h.

Dimer from the Oxidation of 1-(2-Selenienyl)-2-propyn-1-ol (I). Active manganese dioxide [7.4 g (0.085 mole)] was added in small portions to a solution of 3.1 g (0.017 mole) of I in 70 ml of dry ether. The mixture was stirred under nitrogen for 1 h at the boiling point of the solvent, and the precipitate was filtered and washed repeatedly on the filter with ether. The filtrate was washed with water and dried with $MgSO_4$. The ether was partially evaporated, and the dimer was precipitated with alcohol (brown powder) to give 2.5 g (83%) of a product with mp 200-202°. Found %: C 41.59; H 3.51; Se 45.60; mol. wt. 372 (Rast method). $C_{14}H_{12}O_2Se_2$. Calculated %: C 41.62; H 3.47; Se 45.66; mol. wt. 370. The IR spectrum of the dimer contained an absorption band from a conjugated carbonyl group at 1633 cm^{-1}; $C \equiv C$ bond absorption was absent. The dimer was similarly obtained in a yield of 91% (brown powder) by oxidation of 1-(5-methyl-2-selenienyl)-2-propyn-1-ol (II). This product had mp 211-213°. Found %: C 48.12; H 4.11; Se 39.58; mol. wt. 395. $C_{16}H_{16}O_2Se_2$. Calculated %: C 48.24; H 4.02; Se 39.70; mol. wt. 398.

3-Butyl-5-(2-selenienyl)pyrazole (XIII). A mixture of 0.5 g (0.002 mole) of VIII and 0.26 g (0.002 mole) of hydrazine sulfate in 10 ml of alcohol was heated to the boiling point, and a solution of 0.27 g (0.002 mole) of potassium carbonate in a small amount of water was added. The mixture was heated on a water bath for 3 h, cooled, and poured into water. The resulting precipitate was filtered, washed with water, and recrystallized from alcohol to give 0.48 g (90%) of light-yellow crystals of XIII.

Pyrazoles XIV-XVII were similarly obtained.

3-Phenyl-5-(5-bromo-2-selenienyl)isoxazole (XVIII). A mixture of 1.5 g (0.004 mole) of XI and 0.28 g (0.004 mole) of hydroxylamine hydrochloride in 10 ml of alcohol was heated to the boiling point, and a small amount of water was added. A solution of 4.2 g (0.004 mole) of sodium carbonate in a small amount of water was added dropwise. The mixture was heated on a water bath for 3 h and poured into water. The precipitate was filtered, washed with water, and recrystallized from aqueous alcohol to give 1.26 g (80%) of yellow crystals of XVIII.

Isoxazoles XIX-XXI were similarly obtained.

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