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SYNTHESIS OF 2-(2-SELENIENYL)PYRROLE FROM METHYL-2-SELENIENYLKETOXIME AND ACETYLENE

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The reaction of methyl-2-selenienylketoxime with acetylene in KOH—DMSO gives 2-(2-selenienyl)pyrrole and its 1-vinyl derivative.

2-Hetarylpyrroles are important starting materials for synthesizing biologically active compounds in addition to interesting models for studying conjugation effects and internal rotation of two different interacting π-systems [1-3]. In 2-(2-furyl)- and 2-(2-thienyl)pyrroles, such conjugation changes the reactivity of the α-positions toward electrophiles by several orders of magnitude compared with that of the corresponding unsubstituted five-membered heterocycles [3]. The limited number of such compounds, in particular the difficultly accessible Se analogs, impedes extended studies in this area.

The goal of the present study was to investigate the possibility of forming pyrrole from methyl-2-selenienylketoxime (I) and acetylene under Trofimov reaction conditions [1] to give 2-(2-selenienyl)pyrrole (II) and 1-vinyl-2-(2-selenienyl)pyrrole (III) and to investigate the spectral properties of the resulting compounds.

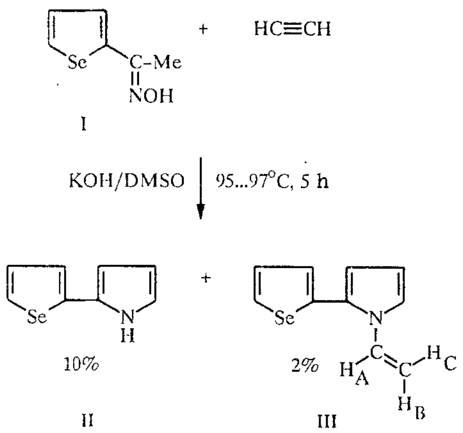

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TABLE 1. Reaction Yields and Pyrrole Yields

T, °C	Time, h	Recovered oxime, %	Yield,* %	
			II	III
95...97	5	55	10	2
110	4	29	8	1
120	10	0	Trace	Trace

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*Per reacted oxime I.

The low yield (Table 1) of II is primarily due to its low stability in KOH—DMSO. Increasing the reaction temperature to 110 °C decreases the yield to 8% and produces polymeric materials. This can be explained by the low stability of the C—Se bond compared with C—O and C—S bonds since the total yield of 2-(2-furyl)- and 2-(2-thienyl)pyrroles and their N-vinyl derivatives under these conditions reaches 80-90% [1].

The starting oxime I consists of a 1:1 mixture of the *syn*- and *anti*-isomers. Under the indicated conditions, predominantly (and only) the *anti*-isomer reacts since the fraction of the *syn*-isomer increases to 77% at the end of the reaction. This agrees with data for formation of pyrrole from methyl-2-benzimidazolylketoxime [4]. At 120 °C both isomers react completely, probably, due to a *syn*⇔*anti* transition.

A comparison of the PMR spectra of the synthesized compounds with those of other N-vinylpyrroles confirms the structure and indicates a significant weak-field shift (0.2-0.5 ppm) [1]. This is consistent with a considerable general shift of π-electrons to the selenophene ring.

The IR spectrum of the pyrrole contains bands assigned to framework stretches at 1530 (s), 1418 (m), and 1384 cm^{-1} (m) [5]. That of the selenophene has bands at 1515 (w), 1423 (s), and 1346 cm^{-1} (m) [6]. The C—H deformations are found at 735 and 758 cm^{-1}, respectively. The IR spectrum of II in these regions contains bands from both heterocycles at 1545 (w), 1502 (m), 1425 (m), 1405 (m), 1380 (m), 1350 (w), 780 (m), and 725 cm^{-1} (s). The vinyl derivative III has bands at 1575 (w), 1530 (w), 1440 (s), 1430 (sh), 1370 (m), 1330 (w), 745 (m), and 705 cm^{-1} (m). The C=C stretch of the vinyl group in III occurs at 1632 cm^{-1}. The free N—H in the pyrrole is at 3460 cm^{-1}. In both II and III, the strong band at 675 cm^{-1} is assigned to C—Se vibrations. The whole series of vibrations of the selenophene and thiophene rings have similar frequencies [7]. The spectrum of II is also very similar to that of 2-(2-thienyl)pyrrole [8].

The UV spectrum (in ethanol) of II has two strong bands near 205 (ε 14,100) and 317 nm (ε 20,300) that are typical of hetarylpyrroles and are assigned to π—π^*-transitions involving the whole π-system [1]. Furthermore, a band is observed at 263 nm (ε 7050) that can apparently be assigned to a perturbed band at 232 nm (ε 3600) that is observed in selenophene [9] and the corresponding transition localized on the selenophene ring. Comparison of the spectra of selenienyl-, thienyl-, and furylpyrrole indicates that the bathochromic shift of the long-wavelength band increases as the polarizability of the heterocycles increases in the sequence 2-furyl (287) < 2-thienyl (305) < 2-selenienyl (317 nm). In contrast with 2-(2-selenienyl)- and 2-(2-thienyl)pyrrole, the long-wavelength band of furylpyrrole has distinct vibrational structure [10]. This may be due to the fact that it does not change in the excited conformation.

EXPERIMENTAL

^1H and ^{13}C NMR were obtained on a Bruker WP 200 SY instrument using resonant frequencies 200.1 MHz (^1H) and 50.3 MHz (^{13}C) at 20 °C. IR spectra were recorded on a Specord IR-75. UV spectra were taken on a Specord UV-Vis.

Methyl-2-selenienylketoxime (I, C_6H_7NOSe). This was prepared from methyl-2-selenienylketone (3.46 g, 0.02 mole), $NH_2OH \cdot HCl$ (2.4 g, 0.04 mole), and NaOH (1.6 g, 0.04 mole) in ethanol (10 ml) at room temperature in 97% yield. Elemental analyses agreed with those calculated. PMR spectrum [in $(CD_3)_2CO$]: 9.74 (OH), 8.35, 7.70, and 7.38 (heterocycle protons), 2.42 (Me_{syn}), 2.31 ppm (Me_{anti}).

2-(2-Selenienyl)pyrrole (II, C_8H_7NSe) and 1-vinyl-2-(2-selenienyl)pyrrole (III). Acetylene was passed for 5 h through a mixture of I (3 g, 0.017 mole) and KOH (1.29 g, 0.031 mole) in DMSO (30 ml) at 95-97 °C. The reaction mixture was diluted 1:2 with water, neutralized with aqueous HCl, and extracted with ether (4×20 ml). After removing solvent, the residue was chromatographed (TLC) on Al_2O_3 using 3:1 hexane—ether as eluent. Yield 0.16 g (5%) II and 0.03 g (1%) III. Oxime I (1.64 g, 55%) was recovered from the mixture. The yield of II per oxime reacted is 10%; of III, 2%. PMR spectrum of II [in $(CD_3)_2CO$]: 10.46 br s (NH), 6.33 (3-H), 6.11 (4-H), 6.82 (5-H), 7.30 (3'-H), $^3J'_{3,4} = 4.0$, $^4J'_{3,5} = 1.5$ Hz, 7.21 (4'-H), $^3J'_{4,5} = 5.8$ Hz, 7.85 ppm (5'-H). ^{13}C NMR spectrum [in $(CD_3)_2CO$]: 129.32 ($C_{(2)}$), 110.2 ($C_{(3)}$), 107.93 ($C_{(4)}$), 119.65 ($C_{(5)}$), 142.82 ($C'_{(2)}$), 122.97 ($C'_{(3)}$), 127.75 ($C'_{(4)}$), 130.85 ppm ($C'_{(5)}$). Signals of vinyl protons in the PMR spectrum of III [in $(CD_3)_2CO$]: 7.14 (H_A, $^3J_{AB} = 8.8$, $^3J_{AC} = 15.6$), 4.80 (H_B, $^2J_{BC} = 1.2$ Hz), 5.33 ppm (H_C).

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