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LETTERS TO THE EDITOR

Stereoselective Addition of Dimethyl Diselenide to Trimethylethynylsilane

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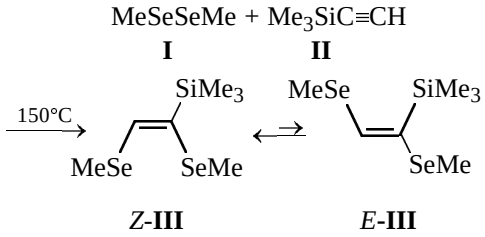
It is known that thermal addition of dialkyl diselenides to alkynes yields 1,2-bis(alkylseleno)-1-alkenes as mixtures of *Z* and *E* isomers with the latter prevailing (the content of the *E* isomer ranges from 64 to 86%) [1]. Thermal addition of dialkyl diselenides to ethynylsilanes was not studied.

We have performed stereoselective thermal (150°C) addition of dimethyl diselenide **I** to trimethylethynylsilane **II**. The reaction affords previously unknown 1-trimethylsilyl-1,2-bis(methylseleno)ethene in 70% yield as a mixture of *Z* and *E* isomers. In contrast to addition of dialkyl diselenides to alkynes [1], predominantly yielding the *E* isomer, the major product of the addition to **II** is the *Z* isomer; its content in the isomer mixture exceeds 95%. Such a high stereoselectivity is unusual for thermal addition to acetylenic compounds.



One of the possible causes of the observed reaction stereoselectivity is the low thermodynamic stability of (*E*)-1-trimethylsilyl-1,2-bis(methylseleno)ethene compared to the *Z* isomer. Apparently, under the conditions of thermal imidization the *Z* and *E* isomers occur in an equilibrium which is shifted toward formation of the *Z* isomer. The low thermodynamic stability of the *E* isomer may be due to strong steric repulsion between the bulky trimethylsilyl group and the methylseleno group in the *cis* position to the $SiMe_3$ group.

Base hydrolysis of **III** yields 1,2-bis(methylseleno)ethene as a mixture of the *Z* and *E* isomers. The isomer ratio is the same as in the starting compound **III**, i.e., the content of the *Z* isomer is about 95%. The spectral characteristics of the *Z* and *E* isomers of 1,2-bis(methylseleno)ethene agree with published data [1, 2].

1-Trimethylsilyl-1,2-bis(methylseleno)ethene III, bp 105–106°C (1 mm). ^{1}H NMR spectrum of the *Z* isomer ($CDCl_3$), δ, ppm: 0.15 s (9H, CH_3Si), 2.13 s (3H, CH_3Se), 2.20 s (3H, CH_3Se), 7.39 s (1H, =CH). Mass spectrum of the *Z* isomer, *m/z* (*I*, %): 288 (27), 193 (8), 153 (18), 123 (10), 93 (11), 83 (21), 73 (100), 45 (28), 43 (29). ^{1}H NMR spectrum of the *E* isomer ($CDCl_3$), δ, ppm: 0.28 s (9H, CH_3Se), 2.11 s (3H, CH_3Se), 2.17 s (3H, CH_3Se), 7.25 s (1H, =CH). Mass spectrum of the *E* isomer, *m/z* (*I*, %): 288 (13), 193 (5), 153 (15), 123 (9), 93 (7), 83 (18), 73 (100), 45 (23), 43 (16). Found, %: C 29.42; H 5.67; Se 54.70; Si 9.66. $C_7H_{16}SeSi$. Calculated, %: C 29.38; H 5.60; Se 55.20; Si 9.82.

The ^{1}H NMR spectra were measured on a Bruker DPX-400 spectrometer (400 MHz, $CDCl_3$, internal reference HMDS). The mass spectra were taken with a Hewlett–Packard 5971A gas chromatograph–mass spectrometer (mass-selective detector, electron impact, ionizing electron energy 70 eV).

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