Preparation of 1-Nitro-1-phenylseleno-1-alkenes

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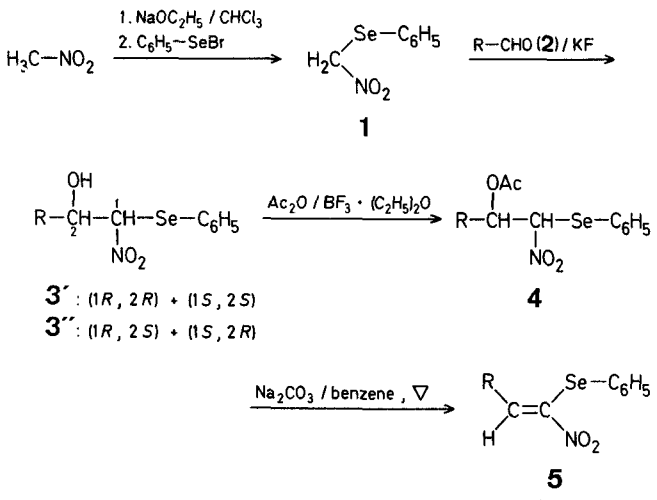
1-Nitro-1-alkenes with hetero atoms at the 1- or 2-position have interesting properties and are often used in organic synthesis. To prepare this class of compounds, groups such as phenylthio and dialkylamino are introduced into the 1-[1] and the 2-position[2] or the 2-position[3], respectively. To our knowledge, preparation of 1-nitro-1-alkenes having a selenenyl group at the 1-position has not been reported. We describe here the synthesis of 1-nitro-1-phenylseleno-1-alkenes **(5)**.

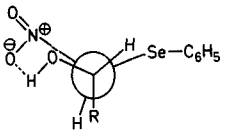


2-5	R	2-5	R
a	n-C_9H_{19}	d	C_2H_5
b	n-C_7H_{15}	e	
c	n-C_4H_9–CH(C_2H_5)–	f	

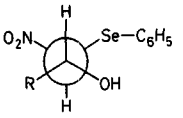
In a previous paper[4], we reported the synthesis of 1-nitro-1-phenylselenoalkanes from 1-nitroalkanes and phenylselenyl bromide. Similar treatment of nitromethane readily affords nitro-(phenylseleno)-methane (**1**) in high yield. This compound is relatively unstable and gradually decomposes to give a fair amount of crystalline diphenyl diselenide after one day even when kept in a freezer under a nitrogen atmosphere.

The Henry addition of **1** with decanal was examined in the presence of various bases [KF, $Pb(CO_3)_2$, $Ca(OH)_2$, Na_2HPO_4, AcONa, $BaCO_3$, $Ba(OH)_2$, pyridine, and triethylamine], of which potassium fluoride gave the most satisfactory results to afford a mixture of **3′a** (36% yield) and **3″a** (52%). These two products were isolated by column chromatography on silica gel; the fast-moving product **3′a** seems to have the (1*R*,2*R*) or (1*S*,2*S*) structure and the slow-moving product **3″a** to have the (1*R*,2*S*) or (1*S*,2*R*) structure as suggested by the data discussed in the following paragraph.

In the I.R. spectrum of **3″a**, the absorption bands of the hydroxy and nitro groups appear at $\nu = 3400$ (broad) and 1545 cm^{-1}, on the other hand, those of **3′a** appear at $\nu = 3520$ (sharp) and 1530 cm^{-1}, respectively; the last value is too low for a saturated nitro group and suggests the presence of a hydrogen bond between the nitro and hydroxy groups. The most appropriate conformation having such a hydrogen bond may be the eclipsed conformation I in which the hydroxy and nitro groups are in the same plane, as observed in 2-nitrophenol. In this conformation, the compound having either the (1*S*,2*S*) or the (1*R*,2*R*) structure should have only little steric hindrance, whereas the compound having (1*S*,2*R*) or (1*R*,2*S*) structures should be destabilized by steric repulsion between the phenylselenenyl and nonyl groups and this destabilization might have a stronger effect than the stabilization due to hydrogen bonding and thus force the conformation into the gauche form II. This speculation is supported by the coupling constants; the $J_{1,2}$ values of **3′a** and **3″a** are 3.5 and 8.0 Hz, respectively. As judged from ^{1}H-N.M.R. spectroscopy, the reaction proceeds slowly and after 12 h the ratio of **3′a** to **3″a** becomes 1:1.1 and does not change further after 4 days.



I (3′a)



II (3″a)

R = n-C_9H_{19}

The reaction of compound **1** with octanal (**2b**) affords the two isomers **3′b** and **3″b** in good yield. The spectral data (I.R. and

Table 1. 1-Nitro-1-phenylseleno-2-alkanols (**3**) prepared

Product	Yield [%]	m.p.[a] or b.p./torr[b] [°C]	Molecular formula[c]	I.R.[d] ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int})[e] δ [ppm]
3′a	36	m.p. 50°	$C_{17}H_{27}NO_3Se$ (372.4)	3520 (sharp OH); 1530 (NO_2)	7.63–7.15 (m, 5H, C_6H_5); 5.42 (d, 1H, J = 3.0 Hz, 1-H); 4.14 (m, 1H, 2-H); 3.11 (br. d, 1H, J = 3.0 Hz, OH)
3″a	52	m.p. 94°	$C_{17}H_{27}NO_3Se$ (372.4)	3400 (br. OH); 1545 (NO_2)	7.66–7.15 (m, 5H, C_6H_5); 5.43 (d, 1H, J = 8.0 Hz, 1-H); 4.01 (m, 1H, 2-H)
3′b	32	m.p. 76°	$C_{15}H_{23}NO_3Se$ (344.3)	3520 (sharp OH); 1530 (NO_2)	7.77–7.28 (m, 5H, C_6H_5); 5.47 (d, 1H, J = 3.5 Hz, 1-H); 4.18 (m, 1H, 2-H); 3.27 (br. s, 1H, OH)
3″b	50	b.p. 170°/0.1	$C_{15}H_{23}NO_3Se$ (344.3)	3420 (br. OH); 1545 (NO_2)	7.72–7.32 (m, 5H, C_6H_5); 5.42 (d, 1H, J = 8.0 Hz, 1-H); 4.03 (m, 1H, 2-H); 2.62 (br. d, 1H, J = 8.0 Hz, OH)
3′c[f]	31	b.p. 141°/0.14	$C_{15}H_{23}NO_3Se$ (344.3)	3550 (br. OH); 1543 (NO_2)	7.60–7.10 (m, 5H, C_6H_5); 5.48 (d, 1H, J = 3.5 Hz, 1-H); 3.96 (m, 1H, 2-H); 2.96 (br. s, 1H, OH)
3″c[f]	49	b.p. 141°/0.14	$C_{15}H_{23}NO_3Se$ (344.3)	3520 (br. OH); 1545 (NO_2)	7.58–7.08 (m, 5H, C_6H_5); 5.46 (d, 1H, J = 8.0 Hz, 1-H); 4.02 (m, 1H, 2-H); 2.46 (s, 1H, OH)
3d	89	[g]	$C_{10}H_{13}NO_3Se$ (274.1)	3450 (br. OH); 1545 (NO_2)	[h]
3e	78	[g]	$C_{14}H_{13}NO_3Se$ (322.1)	3550 (br. OH); 1545 (NO_2)	[h]
3f	83	[g]	$C_{14}H_{12}N_2O_5Se$ (367.1)	3550 (br. OH); 1545, 1525 (NO_2)	[h]

[a] Recrystallized from benzene/cyclohexane.
[b] Kugelrohr apparatus.
[c] Products **3a, b, c** gave satisfactory microanalyses: C, ±0.45; H, ±0.3; N, ±0.25). Compounds **3d, e, f** were not microanalyzed.
[d] The I.R. spectra were recorded on a Hitachi 215 I.R. spectrophotometer as KBr pellets for crystalline products and between NaCl plates for syrupy products.
[e] The ^{1}H-N.M.R. spectra were recorded on a Varian EM-360A spectrometer.
[f] The configuration at C-1 and C-2 was not unambiguously assigned.
[g] Purified by chromatography on a short column.
[h] Complicated ^{1}H-N.M.R. spectrum (mixtures of two isomers).

Table 2. 1-Nitro-1-phenylseleno-1-alkenes (**5**) prepared

Product	Yield [%]	m.p.[a] or b.p./torr[b] [°C]	Molecular formula[c]	I.R.[d] ν_{NO_2} [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int})[e] δ [ppm]
5a	82	b.p. 180°/0.14	$C_{17}H_{25}NO_2Se$ (354.4)	1520	7.59 (t, 1H, J=8.0 Hz, 2-H); 7.48–7.11 (m, 5H, C_6H_5); 2.51 (m, 2H, 3-H)
5b	80	b.p. 167°/0.23	$C_{15}H_{21}NO_2Se$ (326.3)	1520	7.53 (t, 1H, J=8.0 Hz, 2-H); 7.45–7.07 (m, 5H, C_6H_5); 2.35 (m, 2H, 3-H)
5c	88	b.p. 141°/0.14	$C_{15}H_{21}NO_2Se$ (326.3)	1525	7.42–6.90 (m, 6H, C_6H_5+2-H)
5d	88	b.p. 124°/0.24	$C_{10}H_{11}NO_2Se$ (256.2)	1520	7.63 (t, 1H, J=7.5 Hz, 2-H); 7.52–7.18 (m, 5H, C_6H_5); 2.46 (quin, 2H, J=7.5 Hz, 3-H); 1.01 (t, 3H, 4-H)
5e	79	m.p. 58–59°	$C_{14}H_{11}NO_2Se$ (304.2)	1520	8.53 (s, 1H, 2-H); 7.39–7.12 (m, 10H, C_6H_5+C_6H_5)
5f	67	m.p. 55°	$C_{14}H_{10}N_2O_4Se$ (349.2)	1520	8.73 (s, 1H, 2-H); 8.17–7.10 (m, 9H, C_6H_5+C_6H_4)

[a, b, d, e] See Table 1.

[c] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.40; H, ±0.08; N, ±0.10.

^{1}H-N.M.R.) of **3'b** and **3''b** are very similar to those of **3'a** and **3''a**, respectively. The α-branched aldehyde 2-ethylhexanal (**2c**) also reacts with **1** to give two isomeric nitroalcohols **3c** in 31% and 49% yield, respectively. Although the signals of 1-H were observed as doublets with $J_{1,2}$=3.5 Hz for the first eluted isomer (**3'c**?) and with J=8 Hz for the slower moving isomer (**3''e**?), evidence for such hydrogen bonding was not obtained from the I.R. spectra; therefore it is better not to assign the relative configuration at C-1 and C-2 of the two isomeric products **3'c**.

O-Acetylation of nitroalcohol **3'c** (?) with acetic anhydride in the presence of a catalytic amount of boron trifluoride etherate gave the corresponding acetate **(4c)**; however, purification of **4c** by column chromatography or by distillation failed due to partial decomposition. The acetate **4c** was passed through a short column of silica gel to remove diphenyl diselenide and treated with sodium carbonate in boiling benzene to afford the nitroalkene **5c** in good yield. The same nitroalkene was obtained by similar treatment of **3''c** (?). Therefore, there is no need to isolate the isomeric nitroalcohols **3'c** and **3''c** for the preparation of nitroalkene **5c**. In fact, the mixture of **3'c** and **3''c** is converted into nitroalkene **5c** in 88% yield. Similar treatment of **3'a**, **3''a**, or the mixture of **3'a** and **3''a** afforded the nitroalkene **5a** in good yield. The mixture of the nonanols **3'b** and **3''b** was converted into nitroalkene **5b** in 80% yield. However, attempts to prepare nitroalkene **5c** by treatment of the mixture of **3'c** and **3''c** with methanesulfonyl chloride in the presence of triethylamine[5] gave a complex mixture; this is not surprising since the facile formation of double bonds by treatment of β-hydroxyselenides with methanesulfonyl chloride and triethylamine is known[6].

The Henry reaction of **1** with acetaldehyde resulted in the formation of an aldol condensation product instead of the desired nitroalcohol; this may be an exception which is due to the facile formation and the high reactivity of the acetaldehyde anion. In fact, propanal reacts with **1** to give the corresponding nitroalcohol **3d** in 89% yield which is converted into nitroalkene **5d** in 88% yield. Benzaldehyde and 2-nitrobenzaldehyde also undergo the addition reaction with **1** to give the nitroalcohols **3e** and **3f** in 78% and 83% yield, respectively; these alcohols are converted into the nitroalkenes **5e** and **5f** in 79% and 67% yield, respectively.

The nitroalkenes **5** thus prepared were tentatively assigned the (*Z*)-structure on the basis of the ^{1}H-N.M.R. spectra which show strong deshielding of the olefinic proton by the nitro group[7]. We therefore assume that the geometry of the product is controlled by the bulkier nitro group rather than by the phenylseleno group.

Nitro-(phenylseleno)-methane (1):
A 1 molar solution (26 ml, 26 mmol) of sodium ethoxide in ethanol is added to a stirred solution of nitromethane (1.43 ml, 26 mmol) in chloroform (40 ml) whereupon a white precipitate forms. Stirring is continued for 20 min, a solution of phenylselenenyl bromide (4.72 g, 20 mmol) in chloroform (20 ml) is added in one portion, and the mixture is stirred for 1 h and then diluted with water (20 ml). The organic layer is washed with water (2×15 ml), dried with magnesium sulfate, and evaporated. The viscous residue is purified by flash column chromatography[8] with cyclohexane/benzene (9/1) as eluent; yield of **1**: 4.2 g (97%). The product is pure enough for the next reaction. An analytical sample is obtained by distillation in vacuo; b.p. 104°C/0.25 torr.

$C_7H_7NO_2Se$	calc.	C 38.91	H 3.27	N 6.48
(216.1)	found	38.60	3.18	6.30

I.R. (film): ν=1540 cm^{-1} (NO_3).

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ=7.82–7.30 (m, 5H_{arom}); 5.52 ppm (s, 2H, CH_2).

1-Nitro-1-phenylseleno-2-undecanol (3'a and 3''a); Typical Procedure:
A mixture of nitro-(phenylseleno)-methane (**1**; 0.648 g, 3.0 mmol), decanal (**2a**; 1.8 g, 11.5 mmol), and potassium fluoride (10 mg) is stirred for overnight at ~24°C. The mixture is then diluted with water (10 ml) and extracted with chloroform (3×10 ml). The organic extract is washed with water (2×10 ml), dried with magnesium sulfate, and evaporated. The residue is column-chromatographed successively with cyclohexane, cyclohexane/benzene (9/1), and cyclohexane/benzene (4/1) to give small amounts of diphenyl diselenide and **1** as the first fraction. The second fraction is **3'a** together with small amounts of **3''a**. Crystallization from benzene/cyclohexane gives **3'a**; yield: 405 mg (36%). The slow-moving fraction is pure **3''a**; yield: 585 mg (52%); the product gradually crystallizes. An analytical sample is recrystallized from benzene/cyclohexane. For physical properties see Table 1.

3-Ethyl-1-nitro-1-phenylseleno-1-heptene (5c); Typical Procedure:
2-Acetoxy-3-ethyl-1-nitro-1-phenylselenoheptane **(4c)**: To a stirred solution of 3-ethyl-1-nitro-1-phenylseleno-2-heptanol [**3c** (a 1/1.2 mixture of the isomers **3'c** and **3''c**, with the configuration at C-1 and C-2 not assigned; 0.56 g, 1.62 mmol] in acetic anhydride (0.8 ml) is added a catalytic amount (~8 mg) of boron trifluoride etherate at room temperature. Stirring is continued for 15 min and the mixture then poured into ice/water (20 ml) and extracted with chloroform (3×10 ml). The or-

ganic extract is washed with aqueous 30% sodium carbonate (10 ml) and with water (15 ml), dried with magnesium sulfate, and evaporated to give a syrup [I.R. (film): $\nu = 1755\ cm^{-1}$ (OAc)] which is chromatographed on a column (2.5 × 3.5 cm) of silica gel [cyclohexyane/benzene (3:1) as eluent] to remove diphenyl diselenide; yield of crude **4c**: 0.60 g (95%).

3-Ethyl-1-nitro-1-phenylseleno-1-heptene (**5c**): The crude acetate **4c** (0.60 g, 155 mmol) and sodium carbonate (0.3 g) are heated in boiling benzene (20 ml), the reaction being monitored by T.L.C. After disappearance of the acetate **4c** (~6 h), the mixture is filtered and the filtrate concentrated. The residue is column-chromatographed on silica gel (22 g) using cyclohexane/benzene (3/1) as eluent; yield of **5c**: 0.47 g (88%, based on **3c**). The product is pure according to T.L.C. and ^{1}H-N.M.R. analysis. An analytical sample may be prepared by distillation in vacuo; b.p. 141°C/0.14 torr.

When the above conversion is performed with the faster moving isomer **3'c** (0.344 g, 1 mmol) in acetic anhydride (0.5 ml) the yield of acetate **4c** is 0.225 g (84%) and the yield of **5c** is 0.161 g (76%, based on **3c**).

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