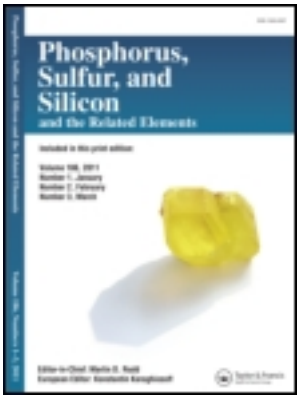

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Syntheses of the Optically Active Terpene Hydroxyphenylselenides

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Syntheses of the Optically Active Terpene Hydroxyphenylselenides

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The optically active hydroxyphenylselenides derived from the p*-menthane, carane, and pinane systems have been obtained. Two methods of hydroxyphenylselenides synthesis have been compared. The first method is based on the reaction of alkenes with* N*-(phenylseleno)succinimide in the presence of water, and the second from epoxides as a result of the reaction with sodium benzeneselenolate. The influence of the substrate structures on the composition of the obtained products has been demonstrated.*

Keywords Epoxides; hydroxyphenylselenides; selenides; terpenes

INTRODUCTION

Recently the synthetic role of the selenoorganic compounds has grown up. Numerous methods using selenoorganic compounds are employed for the synthesis of olefins, alcohols, amines, ethers, heterocyclic systems, and others.[1–4]

In previous articles, we presented syntheses of terpene allyl phenylselenides, convenient precursors for the synthesis of allyl alcohols,[5] allyl toluenesulfonamides,[6–8] and allyl methylcarbamates.[5] Using the optically active allyl phenylselenides, we obtained the respective optically active oxygen and nitrogen derivatives.[5–8]

Herein, we present the syntheses of the optically active terpene hydroxyphenylselenides from the *p*-menthane, carane, and pinane systems. The hydroxyphenylselenides have great synthetic importance and have been used for the synthesis of allyl alkohols,[9] epoxides,[10] amides,[11] dihydroxydiselenides,[12] and diols.[13] The terpene

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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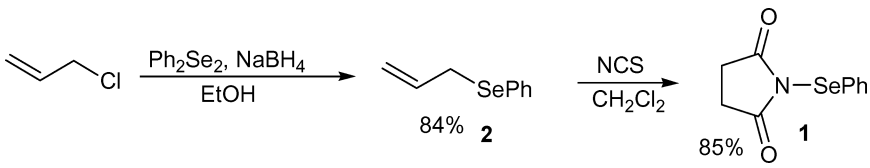


SCHEME 1 Synthesis of *N*-(phenylseleno)succinimide (**1**).

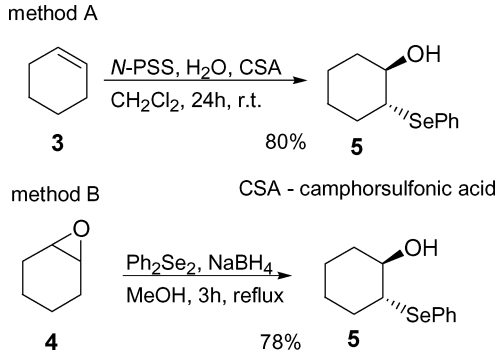
hydroxyphenylselenides from the *p*-menthane series[14,15] have been used as precursors to the isomers of the aggregation pheromone of the ambrosia beetle, *Platypus guercivorus*.[15]

A few methods for the synthesis of hydroxyphenylselenides are known, for example as a result of the reaction of alkenes with phenylselenenyl chloride,[14,16] *N*-(phenylseleno)succinimide (*N*-PSS, **1**),[17] and *N*-(phenylseleno)phthalimide (*N*-PSP)[17] in the presence of water or as the result of the reaction of epoxides with sodium benzeneselenolate.[11]

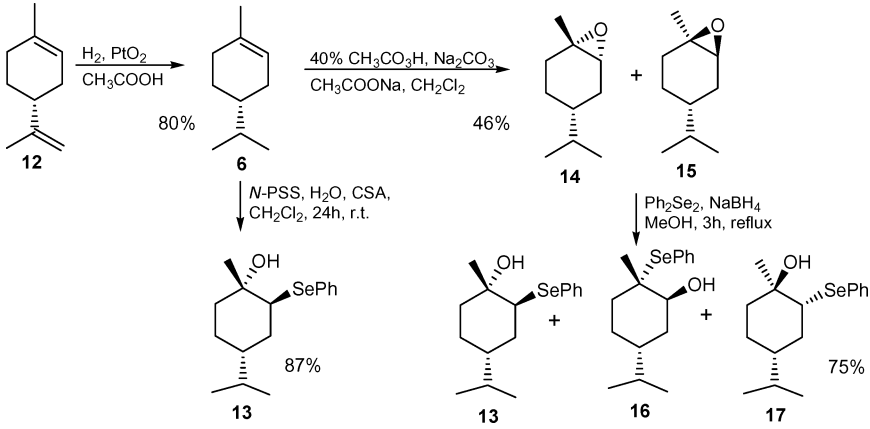
RESULTS AND DISCUSSION

For the synthesis of hydroxyphenylselenides, we used two methods: the addition of *N*-PSS (**1**) to alkenes in the presence of water (method A) and the opening of the epoxide ring with sodium bezeneselenolate (Ph_2Se_2 $NaBH_4$, MeOH) (method B). *N*-PSS (**1**) was obtained as a result of the reaction of allyl phenylselenide (**2**) with NCS (Scheme 1).[18]

The reaction of cyclohexene (**3**) with *N*-PSS (**1**) in the presence of water or cyclohexene oxide (**4**) with sodium benzeneselenolate, hydroxyphenylselenide **5** was obtained in the comparable yields (ca. 80%) (Scheme 2).



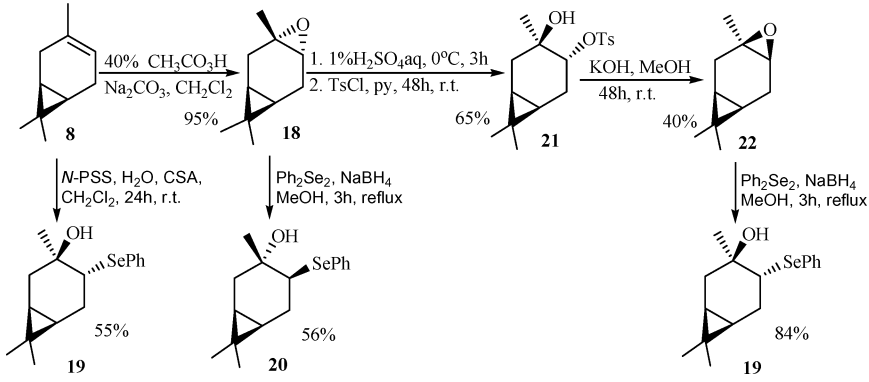
SCHEME 2 Syntheses of hydroxyphenylselenide **5**.



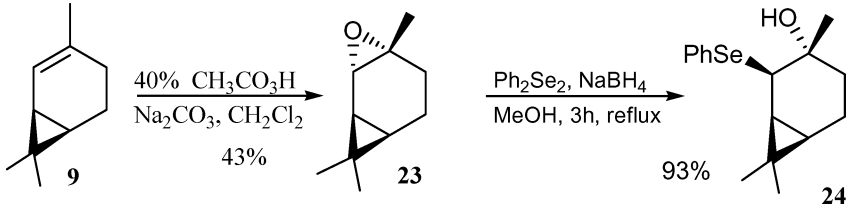
SCHEME 3 Syntheses of hydroxyphenylselenides from *p*-menthane group.

The chosen methods have been used for a synthesis of the optically active hydroxyphenylselenides derived from (+) – *p*-menthene (**6**), (−)-*p*-menthene (**7**), (+)-3-carene (**8**), (+)-2-carene (**9**), (+)-α -pinene (**10**), and (−)-β -pinene (**11**).

(+)-*p*-Menthene (**6**) was obtained by the reduction of (+)-limonene (**12**) with hydrogen in the presence of PtO_2 catalyst. (+)-*p*-Menthene (**6**) with *N*-PSS (**1**) and water gave hydroxyphenylselenide **13** in 87% yield. The epoxidation of (+)-*p*-menthene (**6**) with 40% peracetic acid[19] led to the *cis* and *trans* mixture of *p*-menthene oxides **14** and **15** in a 1:1 ratio. The reaction of the epoxide ring opening was carried out on the mixture of epoxides. Three hydroxyselenides **13**, **16**, and **17** have been



SCHEME 4 Syntheses of hydroxyphenylselenides from (+)-3-carane series.

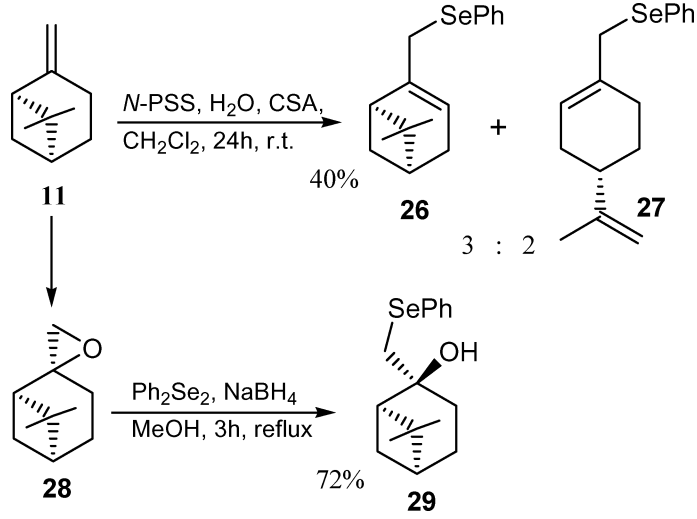


SCHEME 5 Synthesis of hydroxyphenylselenide **24** from (+)-2-carene.

obtained in 75% yield (5.4:2.8:1.8 ratio) (Scheme 3). The same three hydroxydiselenides were obtained by Mori.[15] The analogous results we obtained for (-)-*p*-menthene (**7**).

For the reaction of (+)-3-carene (**8**) with *N*-PSS (**1**) and 3-carene *trans*-oxide (**18**) with sodium benzeneselenolate, hydroxyphenylselenides **19** and **20** have been obtained respectively, in 55% and 56% yield. The application of the (+)-carene *cis*-oxide (**22**) gave the hydroxyphenylselenide **19,** in 84% yield. The (+)-3-carene *cis*-oxide (**22**) have been obtained by the method of Kuczyñski and Chabudziñski[20] as the result of the three-step synthesis, by the epoxide ring opening of the (+)-3-carene *trans*-oxide with the 1% solution of sulfuric acid, a synthesis of the hydroxytosylate **21**, and the repeated closing of the ring to the *cis*-oxide **22** (Scheme 4).

The reaction of (+)-2-carene (**9**) with *N*-PSS (**1**) failed. Instead, the initial alkene **9** was isolated. The opening of the epoxide ring of the



SCHEME 6 Synthesis of hydroxyphenylselenide from (−)-β -pinene.

(+)-2-carene oxide (**23**) by means of the sodium benzeneselenolate gave the hydroxyphenylselenide **24** in 93% yield (Scheme 5).

The reactions of α-pinene (**10**) with *N*-PSS (**1**) and α -pinene oxide with sodium benzeneselenolate failed.

Under the action of *N*-PSS (**1**) on (-)-β -pinene (**11**), a mixture of two phenylselenides was obtained. On the basis of the ^{1}H and ^{13}C NMR spectra and a comparison with the data in the literature,[6,8] it was determined that they correspond to two compounds: 10-phenylseleno-2-pinene (**26**) and 10-phenylseleno-*p*-menthadien (**27**) (3:2 ratio, 40% yield). The analogous results have been obtained by Sharpless.[18] The reaction of the β -pinene oxide (**28**) with sodium benzeneselenolate gave the hydroxyphenylselenide **29** in 72% yield (Scheme 6).

CONCLUSION

Hydroxyphenylselenides from the *p*-menthane, pinane, and carane systems were obtained. All bicyclic terpene hydroxyphenylselenides have been obtained for the first time. The reaction with *N*-PSS and water was the most selective method for the *p*-menthane system. It was established that for bicyclic terpenes under investigation the reaction with sodium benzeneselenolate is the most convenient method.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300, Varian Gemini 200 spectrometers at 300 and 200 MHz, respectively (*J* values are given in Hz). Optical rotations were measured in a 50 mm cells with a polAAr 3000 polarimeter. Column chromatography was performed with Merck silica gel 60 (70–230 mesh). All reactions were carried out under an argon atmosphere.

General Procedure for Method A

To the mixture of *N*-(phenylseno)succinimide (2.28 g, 9 mmol), methylene chloride (16 mL) and cyclohexene (0.82 g, 10 mmol), the solution of camphorsulphonic acid (0.23 g, 1 mmol) in methylene chloride (25 mL), and water (1 mL) were added. The mixture was stirred 3.5 h under argon. To the reaction mixture water (100 mL) was added, the organic layer was separated and aqueous layer was extracted with methylene chloride and dried over anhydrous $MgSO_4$. The solvent was removed to give the oil product, which was purified by means of chromatographic column (silica gel, hexane, then $CHCl_3$) to give the product (1.83 g, 80% yield).

General Procedure for Method B

To diphenyldiselenide (2.50 g, 8 mmol) dissolved in methanol (50 mL), $NaBH_4$ (1.0 g, 26 mmol) was added to decolorization of the reaction mixture. The cyclohexene oxide (1.7 g, 17 mmol) was added and heated under reflux for 3 h. After cooling, water (25 mL) was added, and the reaction mixture was extracted with petroleum ether (120 mL). The organic layer was separated and dried on anhydrous $MgSO_4$. The solvent was removed and the product was purified by means chromatographic column (silica gel, hexane, then $CHCl_3$) to give product (3.18 g, 78% yield).

2-(Phenylselanyl)cyclohexanol (5)

Yield 80%; oil;^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.11–1.50 (m, 4H), 1.52–1.80 (m, 2H), 2.04–2.26 (m, 2H), 2.80–3.07 (m, 2H), 3.24–3.42 (m, 1H), 7.20–7.40 (m, 3H), 7.52–7.64 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.4 (CH_2), 26.7 (CH_2), 33.3 (CH_2), 33.9 (CH_2), 53.4 (CH), 72.2 (CH), 126.7 (C), 127.9 (CH), 128.9 (2xCH), 135.9 (2xCH); ^{77}Se (38 MHz, $CDCl_3$): δ = 337.2.

(1S,2S,4R)-4-Isopropyl-1-methyl-2-(phenylselanyl) cyclohexanol (13)

Yield 87%; oil; $[\alpha]_D^{20}$ +107.1 (c 5.3, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (d J = 6.4 Hz, 3H, CH_3), 0.87 (d, J = 6.6 Hz, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.40–2.20 (m, 9H), 3.40 (t-like, 1H, CH), 7.20–7.35 (m, 3H), 7.52–7.68 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.9 (CH_3), 20.0 (CH_3), 24.7 (CH_2), 29.2 (CH_3), 30.9 (CH), 32.3 (CH_2), 35.1 (CH_2), 38.9 (CH), 54.8 (CH), 72.7 (C), 127.3 (CH), 128.9 (CH), 130.6 (C), 134.2 (CH); ^{77}Se (38 MHz, $CDCl_3$): δ = 359.2.

(1S,3R,4R,6R)-3,7,7-Trimethyl-4-(phenylselanyl) bicyclo[4.1.0]heptan-3-ol (19)

Yield 84%; oil; $[\alpha]_D^{20}$ = –87.7 (c 11.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.58–0.98 (m, 2H, CH), 0.98 (s, 6H, CH_3), 1.29 (s, 3H, CH_3), 1.28–1.36 (m, 1H, CH), 2.09–2.50 (m, 3H), 2.58 (bs, 1H, OH), 3.05 (dd, J = 7.2 Hz, J = 12.4 Hz, 1H), 7.22-7.30 (m, 3H), 7.57–7.65 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.2 (CH_3), 17.5 (C), 20.2 (CH), 20.4 (CH), 23.2 (CH_3), 28.6 (CH_3), 29.7 (CH_2), 33.4 (CH_2), 57.6 (CH), 71.4 (C), 127.1 (CH), 128.9 (CH), 130.1 (C), 133.4 (CH);^{77}Se (38 MHz, $CDCl_3$): δ = 332.1.

(1S,3S,4S,6R)-3,7,7-Trimethyl-4-(phenylselanyl) bicyclo [4.1.0]heptan-3-ol (20)

Yield 55%; oil;$[\alpha]_D^{20} = +77.8$ (c 7,0 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.69–0.80 (m, 2H), 0.99 (s, 6H, CH_3), 1.30 (s, 3H, CH_3), 1.30–1.40 (m, 2H), 1.96–2.09 (m, 1H); 2.22–2.45 (m, 2H), 3.38–3.43 (dd, J = 5.4Hz, J = 10.2 Hz 1H), 7.22–7.30 (m, 3H), 7.54–7.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 18.1 (CH), 18.5 (C), 22.7 (CH), 26.6 (CH_2), 28.2 (CH_3), 28.5 (CH_3), 33.0 (CH_2), 53.9 (CH), 72.5 (C), 127.2 (CH), 128.9 (CH), 130.3 (C), 133.8 (CH); ^{77}Se (38 MHz, $CDCl_3$): δ = 355.2.

(1S,2R,3R,6R)-3,7,7-Trimethyl-2-(phenylselanyl)bicyclo [4.1.0]heptan-3-ol (24)

Yield 93%; oil; $[\alpha]_D^{20} = -201.8$ (c 3.1 $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75–0.88 (m, 1H), 0.98 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.25–1.75 (m, 4H), 1.93–2.10 (m, 1H), 2.11–217 (bs, 1H, OH), 4.05 (dd, J = 1.8 Hz, J = 10.2 Hz, 1H), 7.22–7.30 (m, 3H), 7.58–7.64 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0 (CH_2), 17.1 (CH_3), 21.1 (CH), 22.0 (C), 25.3 (CH), 28.5 (CH_3), 30.1 (CH_3), 32.3 (CH_2), 52.2 (CH), 72.6 (C), 126.8 (CH), 128.9 (CH), 132.6 (C), 133.5 (CH);^{77}Se (38 MHz, $CDCl_3$): δ = 370.9.

(1R,2S,5S)-6,6-Dimethyl-2-(phenylselanylmethyl)bicyclo [3.1.1.]heptan-2-ol (29)

Yield 72%; oil; $[\alpha]_D^{20}$= –55.4 (c 7.6 $CHCl_3$)^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.52 (d, J = 9.8 Hz, 1H) 1.70–2.25 (m, 7H), 2.40 (bs, 1H, OH), 3.29 (d, J = 3.6 Hz, 2H), 7.20–7.32 (m, 3H), 7.50–7.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.3 (CH_3), 24.9 (CH_2), 27.2 (CH_3), 27.3 (CH_2), 30.7 (CH_2), 37.9 (C), 40.7 (CH), 45.1 (CH_2), 51.7 (CH), 75.7 (C), 127.1 (CH), 129.1 (CH), 130.9 (C), 133.2 (CH); ^{77}Se (38 MHz, $CDCl_3$): δ = 234.6.

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