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Photoreductive Cleavage of Phenyl-Selenium Bonds of Phenylselenoalkanes.

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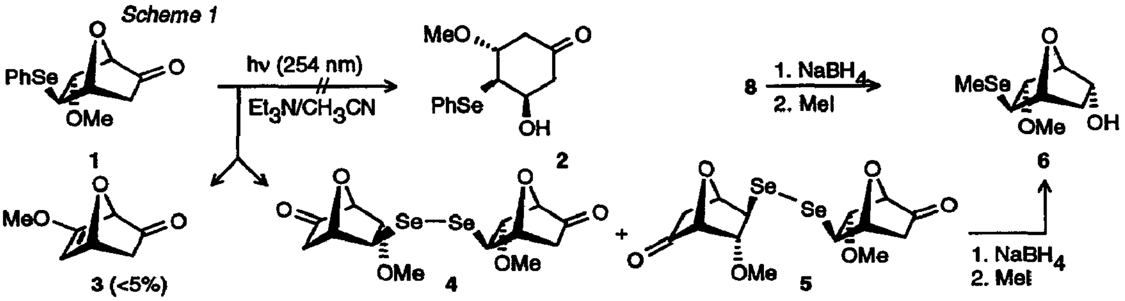
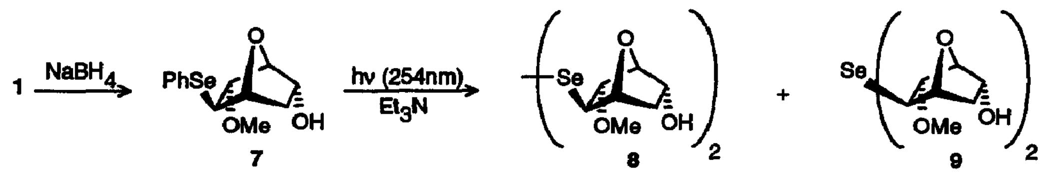
***Abstract:** Photo-induced-electron transfer from triethylamine to phenylselenoalkanes can lead to selective reduction and cleavage of the Ph-Se bond leading to the formation of benzene and the corresponding alkylselenyl radicals that dimerize.*

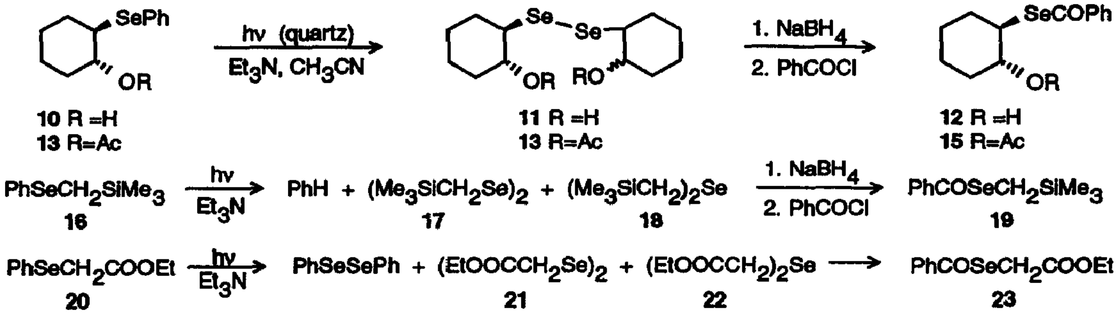
Because the carbon-selenium bond dissociation enthalpy is larger for aryl-Se than for alkyl-Se bonds, chemical[1] and photochemical[2] activation of arylselenoalkanes leads usually to preferential cleavage of the alkyl-Se rather than the aryl-Se bond.[3] We report here that selective cleavage of the phenyl-selenium bond of phenylselenoalkanes can be achieved under photo-induced reductive conditions.[4] The method can be applied to polyfunctional systems including γ-phenylselenoketones.



During the course of our studies on the chemistry of the "naked sugars" and their derivatives[5] we explored the possibility to carry out the ethereal ring opening of the polysubstituted 7-oxanorbornanone 1[5b] into the cyclohexanone derivative 2 under the conditions of Cossy.[6] It was expected that the photo-induced electron transfer from Et$_3$N to 1 would generate the corresponding ketyl radical-anion that would isomerize with cleavage of the C(1)-O(7) bond.[6] The irradiation (quartz vessel, low pressure Hg lamp, Graentzel apparatus, Ar degassed CH$_3$CN, 20°C) of 1 (0.03 molar) in the presence of Et$_3$N (0.15 molar) led to less than 5% of the product of PhSeH elimination 3 and to a 1:1 mixture of the diselenides 4 and 5 (50% yield for 70-80% conversion of 1). To our surprise (Scheme 1), no trace of the ring-opened product 2 could be detected in the crude reaction mixture. Reduction of 4 + 5, which could be separated by column chromatography on silica gel, with NaBH$_4$ in EtOH (20°C, 30 min) followed by the addition of an excess of MeI afforded the methylseleno derivative 6 (55%). The same compound was obtained in the following way. Reduction of 1 with NaBH$_4$ in (THF/MeOH 1:1, 20°C) gave the *endo* alcohol 7 (98%), the irradiation of which (as above) provided a mixture of the diselenides 8 (30-40%) and of the dialkylselenides 9 (30-40%, by ^{1}H-NMR). Treatment with NaBH$_4$/EtOH (20°C, 30 min), then with an excess of MeI (20°C, 15 h) gave, after column chromatography on silica gel, **9** (24%) and **6** (24%).[7] In order to test the generality of the selective phenylselenium bond cleavage process uncovered here, the following experiments were carried out.

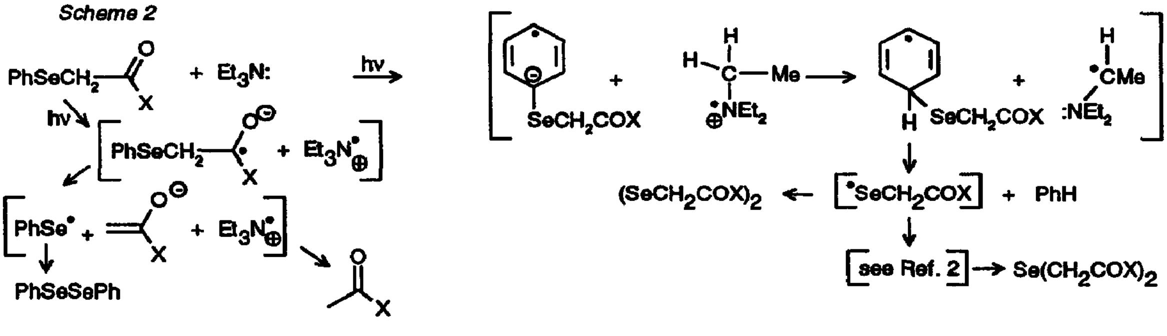


Under the above conditions *trans*-2-phenylselenocyclohexanol (**10**) gave a mixture containing the diselenides **11** (>65% by ^{1}H-NMR) and an unknown olefinic compound (minor). Treatment of the crude reaction mixture with $NaBH_4$ (EtOH, 20°C, 30 min) and then with benzoyl chloride in excess (20°C, 15 h) gave, after chromatographic separation, the expected selenobenzoate **12** the acetylation (Ac_2O, pyridine, 4-dimethylaminopyridine, 20°C, 14 h) of which afforded **15**.[9] The same compound was derived in 12% yield from *trans*-2-phenylselenocyclohexyl acetate (**13**)[8] by photoreduction followed by treatment with $NaBH_4$ and PhCOCl.



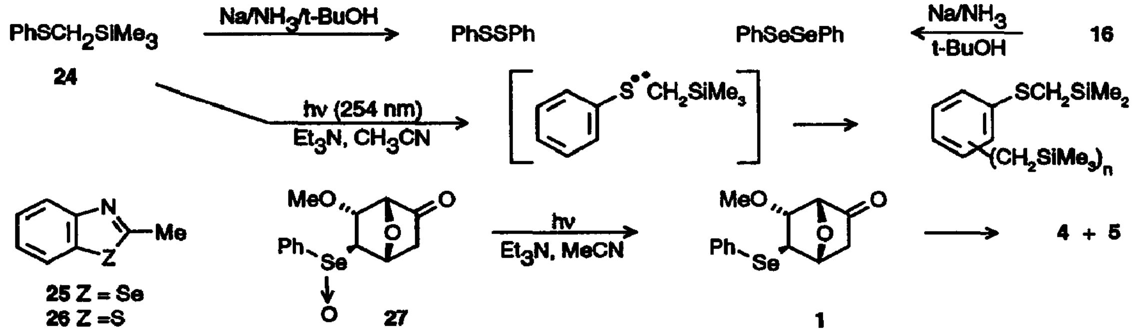
The photoreduction of the silyl derivative **16**[10] gave (>73% by ^{1}H-NMR) a mixture of diselenide **17** (major) and selenide **18** (minor). In this case the formation of benzene was proven by ^{1}H-NMR and ^{13}C-NMR. Treatment of the crude reaction mixture with $NaBH_4$ in EtOH and then with PhCOCl allowed one to isolate (column chromatography on silica gel) the known selenide **18**[11] (25%) and the selenobenzoate **19** (35%).[12] Under the above conditions, irradiation of ethyl phenylselenoacetate (**20**)[13] gave a mixture containing the known diselenide **21**[14] (>30%), the selenide **22** (10%), PhSeSePh (40%) and unreacted **20** (15%) which on treatment with $NaBH_4$ and then with PhCOCl allowed one to isolate (flash chromatography on silice gel) the expected selenobenzoate **23** (15%). The formation of phenyl diselenide suggests that the photo-induced electron transfer from Et_3N involves both the phenylseleno and the carboxylic moieties[16] (Scheme 2). The radical anion resulting from the uptake of an electron from the PhSe group is rapidly neutralized by proton transfer form the triethylammoniumyl radical-cation giving an alkylselenocyclohexadienyl radical which cleaves rapidly into benzene and the corresponding alkylselenyl radical, whereas the ketyl radical-anion resulting from electron transfer to the carbonyl group can undergo cleavage of the alkylselenium bond with formation of the corresponding enolate anion and phenylselenyl radical. Interestingly, when 2-phenylselenocyclohexanone was submitted to UV-irradiation in the presence of Et_3N, exclusive formation of PhSeSePh and cyclohexanone was observed. In this case, the photoreduction of the phenylseleno moiety was not competitive!

Scheme 2



With the hope to approach a better understanding of the processes disclosed above we treated **16** under Birch conditions ($Na/NH_3/t$-BuOH) and did not detect any product of Ph-Se cleavage (Scheme 3). The major compound formed was PhSeSePh showing that the alkyl-Se bond was cleaved preferentially under the non-photochemical reductive conditions.[17] Similarly, when trimethyl(phenylthiomethyl)silane (**24**) was treated under Birch conditions, PhSSPh was formed and isolated in 82% yield. When irradiated with Et_3N, **24** gave a mixture of products resulting from the intermolecular transfer of trimethylsilylmethyl radical. No trace of product resulting from the phenyl-sulfur bond cleavage could be detected (Scheme 3). Under the above photoreductive conditions the selenazole **25** and the thiazole **26** were perfectly stable. Interestingly, irradiation of the selenoxide **27**, led to fast reduction into the phenylselenoalkane **1** which was finally reduced into the diselenides **4** + **5** (Scheme 1).

Scheme 3



Under chemically-induced electron transfer conditions (e.g. HMPA/Na) arylselenoalkanes are cleaved by the alkyl-selenium bond and furnish the corresponding selenophenols.[17,18] To our knowledge the reduction of the phenyl selenium bond had never been reported thus far; our preliminary results suggest that photochemical conditions are necessary to carry out this reaction. An example of aryl-sulfur cleavage has been reported by Tiecco and co-workers[19] with the reaction of hexakis(isopropylthio)benzene and *i*-propylSNa in DMF which provided some pentakis(isopropylthio)benzene. Work is underway in our laboratory to improve the yield of the photo-induced selective reduction of phenylselenoalkane Ph-Se bond and to search for synthetic applications of this reaction.

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7. Data of **6**: yellow oil; IR (CH_2Cl_2): ν 3490, 2600, 1730, 1370, 1080 cm^{-1}; ^1H-NMR ($CDCl_3$, 400 MHz): δ_H 4.47 (d, ^3J=6, H-4), 4.40 (m, H-6), 4.38 (t, ^3J=4.5, H-1), 4.16 (d, ^3J(OH,H-6)=10.8, OH); 4.12 (m, H-2), 3.52 (s, MeO), 2.92 (d, ^3J=3, H-3), 2.49 (m, H-5$_{exo}$), 2.10 (s, MeSe), 1.46 (dd, ^2J=13, ^3J=4, H-5$_{endo}$); ^{13}C-NMR ($CDCl_3$, 101 MHz): δ_C 92.6 (d, ^1J(C,H)=153), 84.6 (d, 162), 74.7 (d, 156), 59.4 (q, 143), 45.8 (d, 146), 40.8 (t, 133), 4.3 (q, 141); CI-MS (NH_3): m/z 238 (16, $M^{+\cdot}$), 207 (4), 138 (12), 111 (100).
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9. Data of **15**: yellow oil; IR (CH_2Cl_2): ν 2920, 1710, 1350; ^1H-NMR ($CDCl_3$, 400 MHz): δ 8.0-7.4 (m, 5 H), 5.13 (m, H-1), 4.10 (m, H-2), 2.00 (s, Ac), 2.0-1.4 (m, 8 H); ^{13}C-NMR ($CDCl_3$, 101 MHz): δ 194.3 (s), 170.3 (s), 139.1 (s), 133.5 (d, 162), 128.7 (d, 163), 127.1 (d, 162), 72.9 (d, 150), 45.3 (d, 146), 30.3 (t, 130), 23.8 (t, 127), 21.4 (t, 130), 21.2 (q, 128); MS (70 eV): m/z 325 (0.2, $M^{+\cdot}$), 122 (3), 106 (100).
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12. Data of **19**: yellow oil; IR (CH_2Cl_2): ν 2940, 1710, 1670, 1190, 1170, 1100, 1020 cm^{-1}; ^1H-NMR ($CDCl_3$, 400 MHz): δ_H 7.93 (m, 2 H), 7.43-7.60 (m, 3 H), 2.21 (s, CH_2), 0.13 (s, Me_3Si); ^{13}C-NMR ($CDCl_3$, 101 MHz): δ_C 195.4 (s), 139.1 (s), 133.4 (d, 162), 128.7 (d, 163), 127.0 (d, 163), 9.0 (t, 132), -1.3 (q, 119); CI-MS (NH_3) m/z: 272 (3, $M^{+\cdot}$), 271 (1), 257 (10), 105 (100), 77 (40).
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15. Data of **23**: yellow oil; IR (CH_2Cl_2): ν 2915, 2830, 1670, 1190, 1170, 870 cm^{-1}; ^1H-NMR ($CDCl_3$, 400 MHz): δ_H 7.90-7.40 (m, 5H), 4.20 (q, ^3J=7.1, CH_2(ethyl)), 3.83 (s, CH_2), 1.27 (t, ^3J=7.1, CH_3(Et)); ^{13}C-NMR ($CDCl_3$, 101 MHz): δ_C 192.2, 170.1 (2s), 134.0 (d, 162), 128.9 (d, 162), 127.2 (d, 160), 61.6 (t, 144), 25.4 (t, 145), 14.0 (q, 127); CI-MS (NH_3): m/z 273 (0.6, $M^{+\cdot}$), 227 (2), 122 (4), 105 (100), 77 (59).
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