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First Isolable *tert*-Alkyl Phenyl Selones

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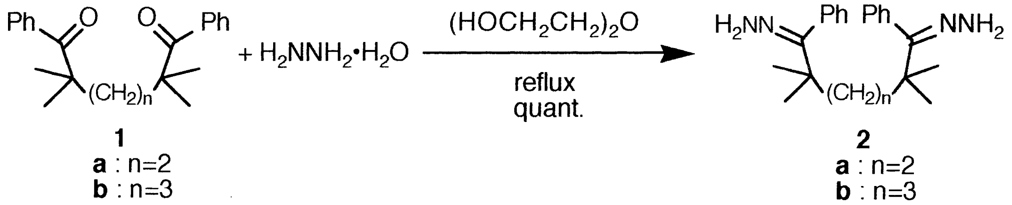
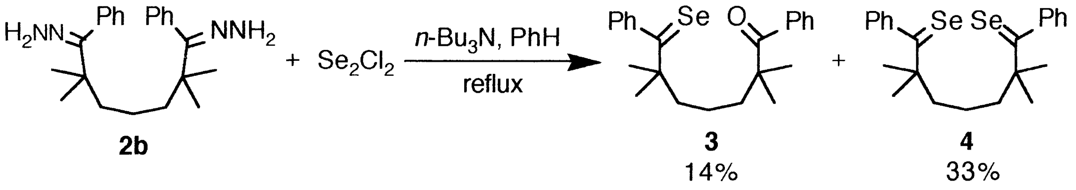
The reaction of the dihydrazone of 2,2,6,6-tetramethyl-1,7-diphenyl-1,7-dione with Se_2Cl_2 in refluxing benzene in the presence of tributylamine gave the corresponding 1-oxo-7-selone and 1,7-diselone derivatives in 14 and 33% yields, respectively, while similar reaction of the dihydrazone of 2,2,5,5-tetramethyl-1,6-diphenyl-1,6-dione gave bicyclic 1,3-diselenetane (25%), 1,2,4-triselenolane (20%), and cyclohexene (12%) derivatives by intramolecular cyclizations.

The chemistry of selenocarbonyl compounds has been attracting much attention.[1,2] It has been recognized that selenoaldehydes and selenoketones (selones) are stabilized by bulky substituents[1a-h] and/or electron-donating substituents.[1i,j] We have recently reported thionation and selenation of nonenolizable α,ω-diketones.[3] During the course of this investigation, we have succeeded in the first preparation of isolable *tert*-alkyl phenyl selones by the reaction of the dihydrazone (**2b**) of 2,2,6,6-tetramethyl-1,7-diphenyl-1,7-dione (**1b**) with Se_2Cl_2.[1e,g] We also report here the reaction of dihydrazone (**2a**) of 2,2,5,5-tetramethyl-1,6-diphenyl-1,6-dione (**1a**) with Se_2Cl_2, which afforded bicyclic 1,3-diselenetane (**5**), 1,2,4-triselenolane (**6**), and cyclohexene (**7**) derivatives.

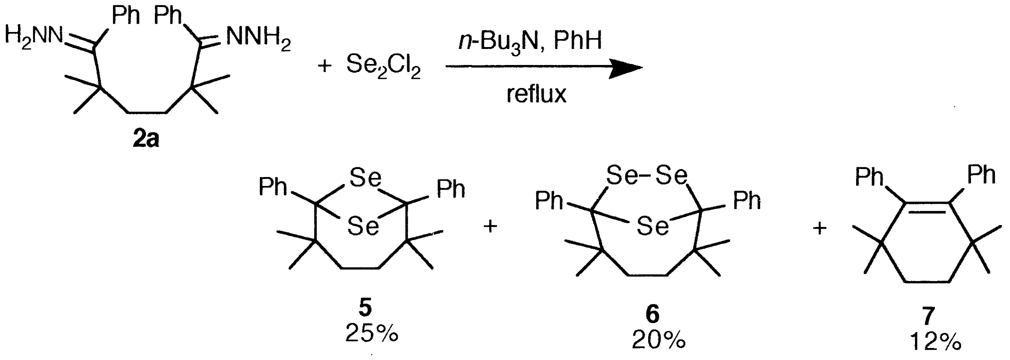
Dihydrazones **2a** and **2b** were quantitatively prepared by the reaction of the corresponding 1,6- and 1,7-diones (**1a** and **1b**) with excess hydrazine monohydrate in boiling diethylene glycol. A solution of 4 molar amounts of Se_2Cl_2 in benzene was added to a solution of dihydrazone **2b** in benzene in the presence of 8 molar amounts of tributylamine and then the mixture was refluxed for 1 h. After the usual workup, purification of the mixture by silica-gel column chromatography provided 2,2,6,6-tetramethyl-1,7-diphenyl-1-oxo-7-selone (**3**) and 2,2,6,6-tetramethyl-1,7-diphenyl-1,7-diselone (**4**) in 14 and 33% yields, respectively.[4]



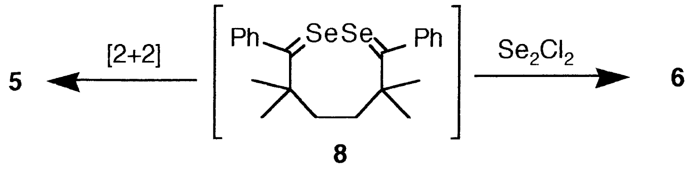


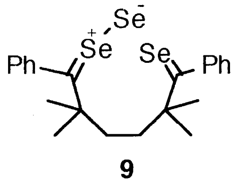
Oily compounds **3** and **4** were blue which is characteristic of selones. They were thermally stable and a fair amount of them remained without decomposition at room temperature after a few months in the dark under air. In the UV-Vis spectra, **3** and **4** showed the maximum absorptions at 688 (ε 98) and 690 (ε 122) nm, respectively. In the ^{13}C NMR, signals due to the selenocarbonyl carbons of **3** and **4** appeared at δ 276.3 and 276.4, respectively. These spectroscopic data clearly indicated the existence of monomeric selenocarbonyl group(s) in **3** and **4**. The compounds **3** and **4** are the first examples of isolable alkyl aryl selones possessing an unsubstituted phenyl group on the selenocarbonyl α-carbon.[1j,5]

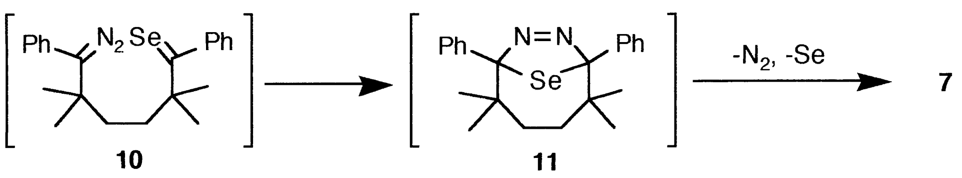
On the other hand, the reaction of dihydrazone **2a** with Se_2Cl_2 in boiling benzene for 6 h gave two bicyclic heterocycles, 1,3-diselenetane **5** (25%) and 1,2,4-triselenolane **6** (20%), and a cyclohexene derivative **7** (12%). No expected selones were detected. Elemental analyses and all spectroscopic data of **5**, **6**, and **7** support the assigned structures.[4]

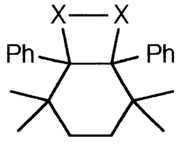


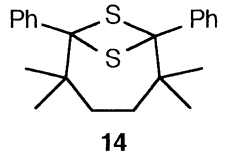
Also in the latter reaction, the diselone **8** must be formed initially, but undergoes intramolecular head-to-tail dimerization to give **5**. 1,2,4-Triselenolane **6** is probably formed by reaction of **8** with Se_2Cl_2.[3b] Although **6** corresponds to an intramolecular cycloadduct of selenoselenine **9**, no supporting evidence for the generation of **9** is available. As to the formation of **7**, intervention of a diazo compound **10** is probable. Oxidation of a sterically hindered hydrazone to the corresponding diazo compound is known.[6] Compound **10** would give rise to **7** by intramolecular cycloaddition followed by two-fold extrusion of N_2 and Se from the resulting 1,3,4-selenadiazoline **11**.[7] An alternative mechanism for the formation of **7** involves intramolecular head-to-head dimerization of selenocarbonyl groups of **8** followed by extrusion of Se_2 from the resulting 1,2-diselenetane **12**. However, this mechanism is less probable because intramolecular cyclization of the dithioxo analog of **1a** to the 1,2-dithietane **13**, which could produce **7** by loss of S_2, is 25.1 kcal mol^{-1} (1 cal=4.184 J) less favorable in enthalpy than that to the 1,3-dithietane **14**.[8]








12 : X=Se
13 : X=S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It is interesting that selones **3** and **4** are stable enough to be isolated at room temperature, whereas **8** is not. The difference in structure between them is only the length of methylene chains (3 methylene chains for **3** and **4**, whereas 2 for **8**), which separate two reactive functional groups. Stability of **3** and **4** should be ascribed to their inability to take an appropriate conformation for undergoing intramolecular head-to-tail dimerization yielding 8-membered ring compounds. The same dimerization of **8** leads to the 7-membered ring compound **5**. 7-Membered ring-forming cyclization is generally more favorable than 8-membered ring-forming one.[9)]

For comparison, we have also examined the reaction of *t*-butyl phenyl ketone hydrazone with Se_2Cl_2 under similar conditions. Although the formation of a blue compound was detected by thin-layer chromatography, it decomposed during the workup. This indicates that $C(CH_3)_2CH_2CH_2CH_2C(CH_3)_2C$(=Se or O)Ph is bulkier than *t*-butyl and thus steric protection of selenocarbonyl by the former is more effective than by *t*-butyl group.

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4) All new compounds gave satisfactory analytical data. Selected spectral data as follows, **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J=7.1 Hz, 2H), 7.46 (t, J=7.4 Hz, 1H), 7.39 (t, J=7.5 Hz, 2H), 7.31 (t, J=7.4 Hz, 1H), 7.21 (t, J=7.7 Hz, 2H), 7.13 (d, J=7.2 Hz, 2H), 1.81-1.77 (m, 2H), 1.68-1.64 (m, 2H), 1.38 (s, 6H), 1.28 (br s, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 276.3 (s), 209.0 (s), 159.7 (s), 139.0 (s), 130.9 (d), 128.1 (d), 127.64 (d), 127.56 (d), 127.1 (d), 121.6 (d), 61.1 (s), 47.9 (s), 42.7 (t), 41.5 (t), 28.8 (q), 26.2

(q), 20.3 (t); MS *m/z* 400 (M$^+$); UV-Vis (hexane) λ_{max} 688 nm (ε 98), **4**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (t, *J*=7.2 Hz, 2H), 7.26-7.18 (m, 8H), 1.82-1.78 (m, 4H), 1.42 (s, 12H), 1.28-1.23 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 276.4 (s), 159.7 (s), 127.8 (d), 127.2 (d), 121.7 (d), 61.1 (s), 42.7 (t), 29.0 (q), 20.2 (t); MS *m/z* 464 (M$^+$); UV-Vis (hexane) λ_{max} 690 nm (ε 122), **5** (pale yellow crystals, mp 143.8-144.5 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (t, *J*=7.5 Hz, 4H), 7.10 (t, *J*=7.4 Hz, 2H), 6.81 (d, *J*=7.9 Hz, 4H), 3.05 (d, *J*=9.8 Hz, 2H), 1.76 (d, *J*=9.6 Hz, 2H), 1.30 (s, 6H), 0.70 (s, 6H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 145.5 (s), 126.6 (d), 126.1 (d), 126.0 (d), 42.3 (s), 41.0 (t), 38.7 (s), 26.0 (q), 21.0 (q); MS *m/z* 450 (M$^+$), **6** (yellow needles, mp 144 °C, dec.): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, *J*=7.3 Hz, 4H), 7.27 (t, *J*=7.5 Hz, 4H), 7.19 (t, *J*=7.3 Hz, 2H), 2.44 (br t, *J*=12.4 Hz, 2H), 1.79 (dd, *J*=10.5, 15.4 Hz, 2H), 1.40 (s, 6H), 0.93 (s, 6H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 144.4 (s), 129.1 (d), 127.2 (d), 126.7 (d), 87.0 (s), 45.2 (t), 36.5 (s), 29.3 (q), 28.1 (q); MS *m/z* 530 (M$^+$), **7** (colorless crystals, mp 144.7-145.0 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.97 (t, *J*=7.3 Hz, 4H), 6.89 (t, *J*=7.3 Hz, 2H), 6.79 (d, *J*=6.8 Hz, 4H), 1.75 (s, 4H), 1.01 (s, 12H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 143.9 (s), 140.9 (s), 130.8 (d), 126.4 (d), 125.0 (d), 36.0 (t), 35.0 (s), 27.0 (q); MS *m/z* 290 (M$^+$).

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