Dihydroselenapyrans by [4 + 2] Cycloaddition of Diaryl Selenoketones

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Received March 8, 1993

Key Words: Selenoketones / Selenapyrans, dihydro / Staudinger chalcogenation / Phosphorus ylides / Cycloaddition

The phosphorus ylides $Ph_3P{=}CAr^1Ar^2$ **5** [Ar^1 = Ph, Ar^2 = 4-$CH_3C_6H_4$ (**c**); $Ar^1 = Ar^2$ = Ph (**d**); 4-ClC_6H_4 (**e**); 4-FC_6H_4 (**f**); 3-$CF_3C_6H_4$ (**g**); Ar^1 = Ph, Ar^2 = 4-ClC_6H_4 (**h**)] were allowed to react with elemental selenium at ca. 75°C in toluene in the presence of an excess of 2,3-dimethylbutadiene. The diaryl selenoketones **1** thus generated in situ by means of the "Staudinger chalcogenation" reaction were trapped by the added conjugated diene to give the 2,2-diaryl-3,6-dihydro-4,5-dimethyl-2*H*-selenapyrans **7** in high yield. Similarly, the ylides **5c–f** and **5h** were treated with selenium, and the resulting diaryl selenoketones **1** added to 1,3-butadiene to give the corresponding 2,2-diaryl-3,6-dihydro-2*H*-selenapyrans **8**. Selenobenzophenone, synthesized analogously, was employed in a [4 + 2] cycloaddition reaction with 2,3-dimethoxybutadiene to yield 3,6-dihydro-4,5-dimethoxy-2,2-diphenyl-2*H*-selenapyran (**9**), which was characterized by an X-ray crystal structure analysis. Compound **9** crystallizes in the space group $P2_1/n$. In the crystal the dihydro-2*H*-selenapyran adopts a distorted half-chair conformation.

There has been a great interest in the chemistry of organic compounds having carbon connected by means of multiple bonds to elements from the second and higher rows of the periodic table[1]. As exemplified by the features of the thio-, seleno-, and tellurocarbonyl group these C=X systems are not to be regarded as simple homologs of their "lighter" congeners (here the ubiquitous organic carbonyl group), but seem to exhibit themselves a characteristic chemistry which has to be explored and developed. Thus, the $R^1R^2C{=}X$ (X = S, Se, Te) compounds are at the same time more nucleophilic (higher HOMO) *and* electrophilic (lower LUMO) as compared to their aldehyde or ketone analogs[2]. The carbon-element π systems in these heterocarbonyl compounds are usually characterized by a very high chemical reactivity. Consequently, the heavier analogs of the organic carbonyl compounds can often not be isolated as such; but they can be generated from various precursors, trapped by means of added scavengers and in this way often utilized synthetically[3].

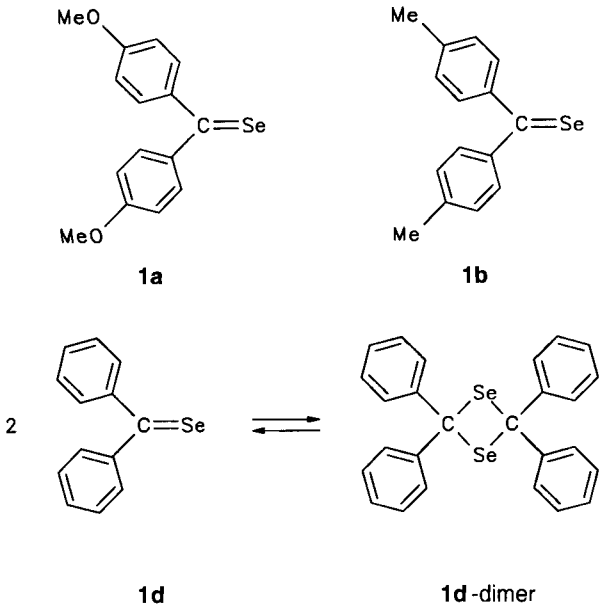
The chemistry of selenoketones and -aldehydes is less developed than the respective thiocarbonyl chemistry. However, there has been remarkable progress in the synthetic chemistry of $R^1R^2C{=}Se$ compounds especially in the last decade. A few remarkable cases have been reported where selenoketones are isolated as stable monomers. Stabilization has been achieved by introducing very bulky substituents (kinetic stabilization as illustrated e.g. by examples described by the groups of Barton, Guziec, or Okazaki[4]), by means of specific electronic stabilization (e.g. by introducing electron-donating substituents into conjugatively active positions relative to the C=Se functionality as shown by Reid[5] or Okuma et al.[13]) or by complexation with transition metals (representative examples have been described e.g. by Roper, Fischer, Werner et al.[6]). Recently, Kirby, Krafft, Segi, Okuma, Takikawa, and others have developed very elegant methods to generate reactive selenoketones or -aldehydes that in most cases have been trapped directly with added conjugated dienes to give the respective dihydro-2*H*-selenapyran systems in high yields[7]. The extremely reactive selenoformaldehyde has been generated (Bock, Moule[8]), and even more reactive analogs containing strongly electron-withdrawing fluorine atoms at the C=Se functionality have been generated and trapped (Grobe, Haas, Roesky et al.[9]).

Our group and Okuma's group have independently found that phosphorus ylides $Ph_3P{=}CR^1R^2$ react with elemental selenium to afford selenoketones and -aldehydes[10,11]. This variant of the "Staudinger chalcogenation" reaction[12] is easy to perform and thus represents a very favorable entry to selenocarbonyl chemistry. Okuma has used this method for the preparation and isolation of stable monomeric 4,4′-dimethoxy- and 4,4′-dimethylselenobenzophenone[13]. We have shown that the parent selenobenzophenone synthesized by this route exists as a stable monomer in solution but rapidly undergoes reversibel [2 + 2] dimerization upon concentration of the solution. Only the dimeric form (**1**-dimer) of selenobenzophenone has been found in the solid state (see Scheme 1)[14].

Selenobenzophenone thus seems to represent an important borderline case. This reactive selenoketone is monomeric in solution but cannot be isolated as such. Attaching stabilizing electron-donating groups (OCH_3, NR_2) leads to isolable monomeric diaryl selenoketones[13]. Consequently, the attachment of electron-withdrawing substituents to the

aromatic rings should result in a marked destabilization of the respective diaryl selenoketone systems. It was expected that the attachment of electronegative halide or haloalkyl groups to the aromatic rings should greatly increase the chemical reactivity of the C=Se functionality in these compounds. Therefore, it had to be investigated whether the generation of such reactive destabilized diaryl selenoketones was still within the scope of the "Staudinger chalcogenation" reaction. We selected a series of Cl-, F-, and CF_3-substituted diaryl selenoketones as targets of our study and employed selected conjugated dienes for trapping the reactive heteroketones with the formation of the respective dihydro-2*H*-selenapyran systems.

Scheme 1



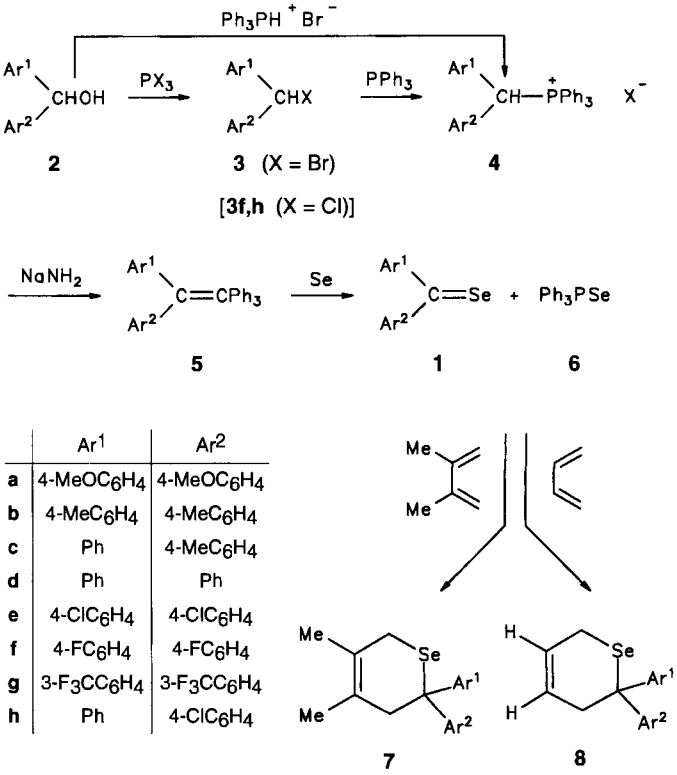
Results and Discussion

Generation of the Diaryl Selenoketones and Trapping with Conjugated Dienes

The phosphorus ylides used for this study were prepared in the usual way by deprotonation of the respective diarylmethylphosphonium halides with sodium amide[15]. The phosphonium salts were usually synthesized by the reaction of the corresponding diarylmethyl halides with triphenylphosphane. The diarylmethyl halides were obtained from commercial sources or synthesized by treatment of the respective diarylcarbinols with PBr_3. In a few cases the reaction of the diarylcarbinol with $Ph_3PH^+X^-$ turned out to be advantageous[16]. All phosphorus ylides employed in this study were isolated and obtained as orange-red to red crystalline materials that were indefinitely stable in an inert atmosphere.

We thus synthesized and isolated the phosphorus ylides **4a-h**. These were then treated with elemental selenium under various reaction conditions. In a first series of experiments each of the ylides was dissolved in toluene. Selenium (ca. two molar equivalents) was added and the mixture was charged with an excess (ca. sevenfold) of the 2,3-dimethylbutadiene scavenger. The mixture was then kept for several hours at 75 °C with stirring. Workup (see Experimental) gave the corresponding 2,2-diaryl-3,6-dihydro-4,5-dimethyl-2*H*-selenapyrans (7) in 63 to 86 % yield.

Scheme 2



	Ar^1	Ar^2
a	4-$MeOC_6H_4$	4-$MeOC_6H_4$
b	4-MeC_6H_4	4-MeC_6H_4
c	Ph	4-MeC_6H_4
d	Ph	Ph
e	4-ClC_6H_4	4-ClC_6H_4
f	4-FC_6H_4	4-FC_6H_4
g	3-$F_3CC_6H_4$	3-$F_3CC_6H_4$
h	Ph	4-ClC_6H_4

The dihydro-2*H*-selenapyrans **7** show characteristic NMR spectra. 2,2-Bis(4-chlorophenyl)-3,6-dihydro-4,5-dimethyl-2*H*-selenapyran (**7e**) thus exhibits ^{13}C-NMR signals at δ 132.3 and 124.7 corresponding to the ring carbon atoms C-4 and C-5. The methyl groups attached to these olefinic carbon centers give rise to resonances at δ 20.6 and 19.7. The ^{13}C-NMR signal of the methylene group adjacent to selenium is observed at δ 24.7 (C-6, $^1J_{CH} = 140$ Hz), whereas the methylene group adjacent to the CAr_2 unit shows a resonance signal at δ 47.3 (C-3, $^1J_{CH} = 128$ Hz). The resonance of C-2 appears at δ 50.4.

In this series of experiments we have generated the following diaryl selenoketones **1** in situ and have trapped them with 2,3-dimethylbutadiene to obtain the corresponding dihydro-2*H*-selenapyran systems **7**: bis(4-chlorophenyl) selenoketone (**1e**), bis(4-fluorophenyl) selenoketone (**1f**), bis[3-(trifluoromethyl)phenyl] selenoketone (**1g**), (4-methylphenyl) phenyl selenoketone (**1c**), and (4-chlorophenyl) phenyl selenoketone (**1h**). For the purpose of comparison we have also prepared the known bis(4-methoxyphenyl) selenoketone (**1a**)[13] by the reaction of $Ph_3P{=}C(C_6H_4OCH_3)_2$ (**5a**) with elemental selenium and have added it to 2,3-dimethylbutadiene to obtain 3,6-dihydro-2,2-bis(4-methoxyphenyl)-4,5-dimethyl-2*H*-selenapyran (**7a**) in 63 % yield. In Table 1 are listed the products and their yields obtained in

this series of experiments as well as their characteristic ^{13}C-NMR data.

Table 1. Selected ^{13}C-NMR data (δ values rel. TMS, in $CDCl_3$) of dihydro-2*H*-selenapyrans **7** obtained by [4 + 2] cycloaddition reaction of differently substituted diaryl selenoketones **1** with 2,3-dimethylbutadiene

Product	Yield (%)	C-2	C-3	C-4/C-5	C-6
7a	63	50.5	48.0	124.3/128.6	24.7
7c	86	51.5	47.6	124.3/128.1	24.6
7e	64	50.4	47.3	124.7/132.3	24.7
7f	75	50.3	47.8	124.6/128.3	24.8
7g	67	51.2	47.1	125.5/128.1	24.9
7h	73	51.1	47.4	124.6/128.4	24.6

Five of the diaryl selenoketones (**1c–f,h**) were also treated with 1,3-butadiene. These experiments were carried out in a slightly different fashion. In each case the corresponding ylide was dissolved in toluene and then treated with an excess of selenium for several hours at 70–85 °C in the *absence* of the conjugated diene scavenger. The resulting light to dark green-colored mixtures were then cooled to −78 °C. Then an excess of 1,3-butadiene was added and the mixture allowed to warm to room temperature. Subsequent workup (see Experimental) gave the respective 2,2-diaryl-3,6-dihydro-2*H*-selenapyrans **8** in good yields (63–76% isolated).

The selenapyrans **8** also show very characteristic NMR spectra. As a typical example 2,2-bis(4-chlorophenyl)-3,6-dihydro-2*H*-selenapyran (**8e**) exhibits an AA'BB' pattern of the hydrogen atoms at the aromatic substituents in the ^1H-NMR spectrum at δ 7.12 and 7.01. The ^1H-NMR signals of the olefinic ring −CH=CH− moiety appear at δ 5.85 and 5.91 (4-H/5-H), the resonances of the ring methylene groups are observed at δ 3.03 and 2.94 (6-H, 3-H). In the ^{13}C-NMR spectrum the olefinic ring carbon atoms of **8e** give rise to signals at δ 124.8 and 129.4 (C-4, C-5). The quaternary ring carbon center shows a resonance at δ 48.8 (C-2). The adjacent ring methylene group exhibits a signal at δ 40.0 (C-3), whereas the methylene group adjacent to the selenium heteroatom gives rise to a ^{13}C-NMR resonance at δ 19.4 (C-6) (in [D_6]benzene). The yields and selected ^{13}C-NMR data of the isolated dihydro-2*H*-selenapyran systems **8** are listed in Table 2.

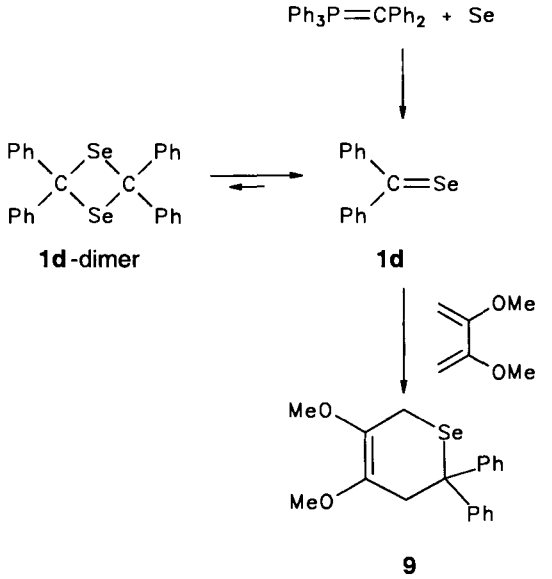
Table 2. Selected ^{13}C-NMR data[a] of dihydro-2*H*-selenapyrans **8** obtained by the reaction of diaryl selenoketones (**1**) with 1,3-butadiene

Product	Yield (%)	C-2	C-3	C-4/C-5	C-6
8c	73	50.2	40.2	124.6/129.9	19.3
8d	63	50.6	40.4	124.8/129.8	19.2
8e	76	48.8	40.0	124.8/128.4	19.4
8f	66	49.1	39.8	124.8/129.2	19.4
8h	69	48.8	40.0	124.7/129.2	19.3

[a] In [D_6]benzene (**8d**, **8e**) or $CDCl_3$, chemical shifts (δ) are given rel. TMS.

Molecular Structure of 3,6-Dihydro-4,5-dimethoxy-2,2-diphenyl-2*H*-selenapyran

The [4 + 2] cycloaddition reaction between selenobenzophenone (**1d**)[14] and 2,3-dimethoxybutadiene was carried out in two different ways. In one experiment the ylide $Ph_3P{=}CPh_2$ (**5d**) was treated with elemental selenium at 85 °C. Then the remaining selenium was filtered off, and the reaction mixture was charged with an excess (ca. eightfold) of 2,3-dimethoxybutadiene. Workup after a reaction time of 24 hours at ambient temperature then gave 3,6-dihydro-4,5-dimethoxy-2,2-diphenyl-2*H*-selenapyran (**9**) in 70% yield.



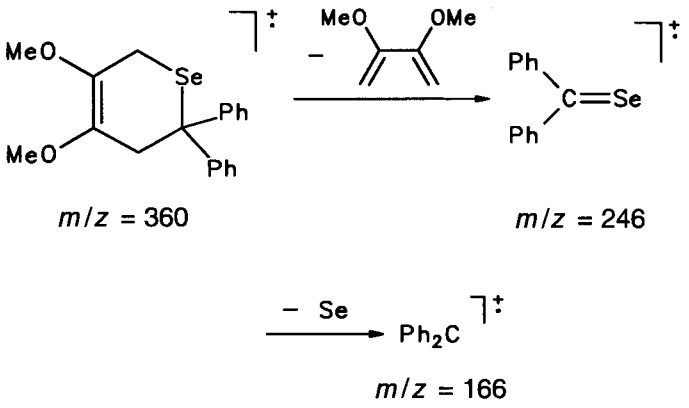
9

In a separate experiment we employed the isolated dimer of selenobenzophenone as the starting material for the cycloaddition reaction. This was possible since we knew from previous experiments that 2,2,4,4-tetraphenyl-1,3-diselenacyclobutane (**1d**-dimer) rapidly equilibrates with the monomeric selenoketone **1d** in solution [**1d**-dimer → 2 (**1d**): $\Delta G^{\neq}$ (323 K) = 24.4 ± 0.3 kcal mol^{-1}][14]. The compound **1d**-dimer was thus dissolved in toluene containing ca. 2.5% of 2,3-dimethoxybutadiene (≈ sixfold molar excess). Workup after a reaction time of 6 hours at ambient temperature furnished the [4 + 2]cycloadduct **9** in nearly 90% yield.

The product **9** exhibits the typical NMR spectra as expected for a dihydro-2*H*-selenapyran system with ^1H-NMR signals at δ 2.82 (6-H) and 3.21 (3-H) and OCH_3 resonances at δ 3.38 and 3.55. The ^{13}C-NMR spectrum of **9** shows the C-6 resonance at δ 17.5 ($^1J_{CH}$ = 142 Hz), whereas the C-3 and C-2 signals are observed at δ 43.7 ($^1J_{CH}$ = 129 Hz) and 51.0. The olefinic carbon centers (C-4, C-5) give rise to signals at δ 138.5 and 142.0; the signals of the attached methoxy groups appear at δ 57.6 and 58.1. In the mass spectrum (EI) compound **9** shows its molecular ion peak at m/z = 360 (7%). The dominant fragmentation pattern leads to the selenobenzophenone molecular ion (m/z = 246, 100%, loss of 2,3-dimethoxybutadiene) with subsequent selenium elimi-

nation to give the Ph_2C molecular ion fragment ($m/z = 166$, 58 %).

The molecular structure of compound **9** in the solid state was determined by X-ray diffraction. Compound **9** crystallizes in the space group $P2_1/n$[17].



In the crystal compound **9** adopts a half-chair conformation of the central heteroatom-containing six-membered ring as is typically observed for cyclohexenes and dihydro-2*H*-pyran derivatives[18]. Relative to cyclohexene itself the heterocyclic half-chair of **9** is somewhat distorted because of the larger covalent atomic radius of the incorporated selenium atom (1.16 Å) relative to carbon (0.77 Å). This leads to an increased displacement of the location of the selenium atom relative to the mean plane defined by the carbon atoms C(2) to C(5). Carbon atom C(1) is also arranged outside of this central plane but located at the face opposite to the selenium atom. The C(3)–C(4)–C(5)–Se dihedral angle is 21.0°, whereas the C(4)–C(3)–C(2)–C(1) dihedral angle is markedly reduced to 16.3°. The corresponding all-carbon atom dihedral angle in the cyclohexene half-chair amounts to 15.7°.

The methoxy oxygen atoms at C(3) and C(4) are oriented in the olefinic mean plane with the attached methyl groups rotated to lie on opposite sides of this plane [dihedral angles C(2)–C(3)–O(1)–C(18): 60.4° and C(5)–C(4)–O(2)–C(19): 106.9°]. The C(3)–C(4) bond is in the typical range of olefinic carbon-carbon double bonds [1.320(4) Å] and the C(3)–O(1) and C(4)–O(2) distances [1.384(4) and 1.390(4)Å] are as expected for O–C(sp^2) single bonds[19]. The distances of adjacent C(sp^2)–C(sp^3) bonds are 1.506(4) [C(3)–C(2)] and 1.478(5) Å [C(4)–C(5)]. They are slightly shorter than the C(2)–C(1) linkage [1.534(4) Å] between two sp^3-hybridized carbon atoms. The corresponding C(1)–C(12) bond is 1.518(4) Å; the adjacent C(1)–C(6) linkage is 1.532(4) Å which is rather long for a C(sp^2)–C(sp^3) connection. The bonds to selenium are 2.000(3) [C(1)–Se] and 1.950(4) Å [C(5)-Se]. The former value is at the high end of the C(sp^3)–Se single bond range [to be compared with typical C–Se distances: 1.980(9) Å: $(CF_3)_2Se$; 1.959(10) Å: CH_3SeH; 1.962(2) Å: C_2H_5SeH; 1.956(5) Å: CH_3SeCN, 1.984(20) Å: CF_3SeCN; 1.957(19) Å: $PhSeCH_3$; 1.954(4) Å: $(CH_3Se)_3B$; 1.975(3) Å: $(CF_3Se)_3N$; 1.975(3) Å: $(CH_2)_4Se$][20]. The C(1)–Se–C(5) angle in **9** is 92.4(1)°.

The averaged angle between the σ bonds at carbon atom C(1) is almost ideally tetrahedral (109.4°). However, a close inspection reveals a rather broad range of individual bond angles at the sp^3-hybridized carbon center C(1), some being larger and others being markedly smaller than 109° [C(12)–C(1)–C(6): 111.0(2)°; C(12)–C(1)–C(2): 114.1(2)°; C(12)–C(1)–Se: 108.0(2)°; C(6)–C(1)–C(2): 108.0(2)°; C(6)–C(1)–Se: 109.7(2)°; C(2)–C(1)–Se: 105.8(2)°]. This strong deviation from C(sp^3)–element bonding angles (here ± 3°) is frequently observed in organic compounds but not usually recognized as being the rule rather than the exception. We thus do not regard some of the bonding angles at the sp^3-hybridized carbon centers C(2) [C(3)–C(2)–C(1): 117.0(3)°] and C(5) [C(4)–C(5)–Se: 113.8(3)°] as untypically large.

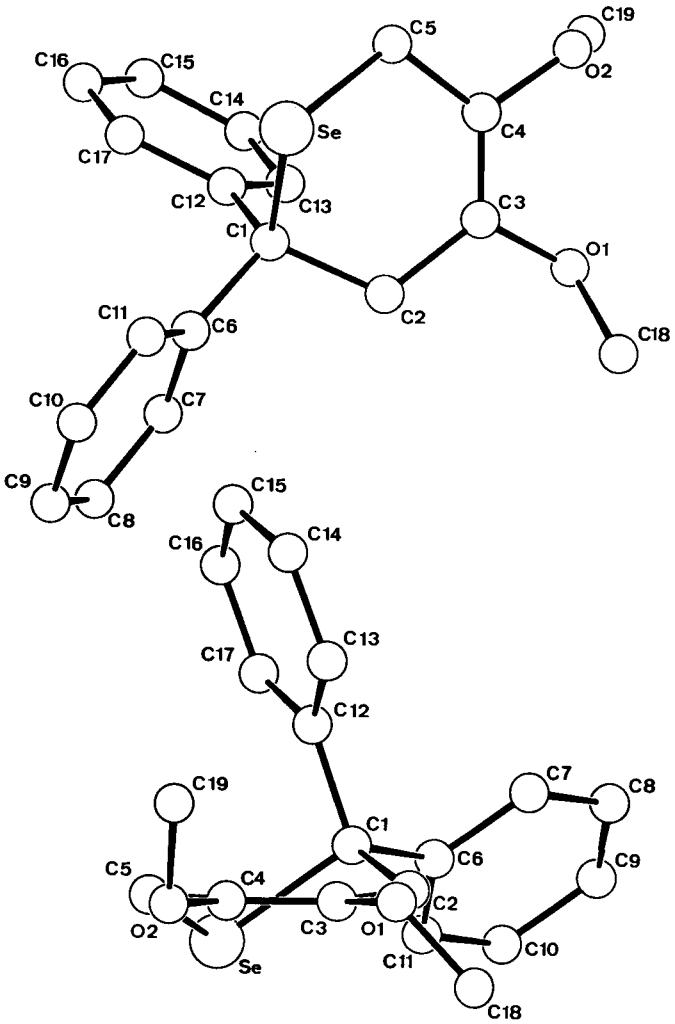


Figure 1. Two views of the molecular structure of the dihydro-2*H*-selenapyran **9** (with unsystematical atom numbering scheme); selected bond lengths [Å] and angles [°]: Se–C(1) 2.000(3), Se–C(5) 1.950(4), O(1)–C(3) 1.384(4), O(1)–C(18) 1.388(6), O(2)–C(4) 1.390(4), O(2)–C(19) 1.428(5), C(1)–C(2) 1.534(4), C(1)–C(6) 1.532(4), C(1)–C(12) 1.518(4), C(2)–C(3) 1.506(4), C(3)–C(4) 1.320(4), C(4)–C(5) 1.478(5); C(5)–Se–C(1) 92.4(1), C(18)–O(1)–C(3) 115.7(3), C(19)–O(2)–C(4) 114.5(3), C(12)–C(1)–C(6) 111.0(2), C(12)–C(1)–C(2) 114.1(2), C(12)–C(1)–Se 108.0(2), C(6)–C(1)–C(2) 108.0(2), C(6)–C(1)–Se 109.7(2), C(2)–C(1)–Se 105.8(2), C(3)–C(2)–C(1) 117.0(3), C(4)–C(3)–C(2) 126.7(3), C(4)–C(3)–O(1) 118.5(3), C(2)–C(3)–O(1) 114.5(3), C(5)–C(4)–C(3) 126.4(3), C(5)–C(4)–O(2) 112.0(3), C(3)–C(4)–O(2) 121.6(3), C(4)–C(5)–Se 113.8(3)

The factual deviation from the expected standard hybridization angles is often even more pronounced at planar-tricoordinate carbon. This is also observed for the heterocycle **9**. The averaged bonding angles at the olefinic carbon atoms C(3) and C(4) are 119.9 and 120.0°, respectively. However, the individual bond angles deviate as much as 6.7° at C(3) and 8.0° at C(4) [C(4)–C(3)–C(2): 126.7(3)°; C(4)–C(3)–O(1): 118.5(3)°; C(2)–C(3)–O(1): 114.5(3)° and C(5)–C(4)–C(3): 126.4(3)°; C(5)–C(4)–O(2): 112.0(3)°; C(3)–C(4)–O(2): 121.6(3)°]. We note that at the trigonally planar carbon atom C(4) the individual C(5)–C(4)–O(2) angle [112.0(3)°] is much closer to the theoretical tetrahedral bonding angle (109°) than to the theoretically expected 120° angle of sp^2-hybridized carbon. Again, we would like to stress that this is probably not an unusual structural situation but that such deviations from idealized bonding geometries at carbon can very often be observed in normal organic compounds[21].

Conclusion

Okuma's and our previous studies have characterized the chemical behavior of selenobenzophenone and diaryl selenoketones bearing electron-donating substituents at the aromatic rings, that serve to diminish the electron-deficiency at the C=Se linkage and thereby appear to increase the overall stability of the selenocarbonyl compounds[10,11,13,14]. The present study has extended the scope of substituted diaryl selenoketones that are easily available by the "Staudinger chalcogenation" synthetic method, i.e. by the reaction of the respective $Ph_3P{=}CAr_2$ ylides with elemental selenium. This method is also applicable to the preparation of diaryl selenoketones bearing strongly electron-withdrawing substitutents at the aromatic nuclei. These probably very reactive diaryl selenoketones can be trapped by added 2,3-dimethylbutadiene in high yields when generated in situ. Our additional series of experiments has shown that these heterocarbonyl compounds can also be added cleanly to 1,3-butadiene itself. In these latter experiments we have not generated the respective selenoketones directly in the presence of the conjugated diene scavenger. The reactive selenoketones are first prepared at high temperature by the reaction of the ylide with the chalcogen. Butadiene is added when this reaction has gone to completion. Even this reaction mode leads to high yields of the respective dihydro-2*H*-selenapyran systems. This means that a reactive form of the diaryl selenoketones having electron-withdrawing substituents attached has remained persistent in solution for some time until the trapping reagent is added. It has to be revealed by further experimental studies whether these are the reactive substituted diaryl selenoketones as such or if they are present in such solutions as their dormant dimeric forms (or an equilibrium of these two). In any case our study has shown that the "Staudinger chalcogenation" of phosphorus ylides can be used to make a variety of differently substituted diaryl selenoketones available for synthetic purposes such as e.g. the preparation of substituted dihydro-2*H*-selenapyran ring systems.

Financial support from the *Fonds der Chemischen Industrie*, the *Deutsche Forschungsgemeinschaft*, and the *Alfried Krupp von Bohlen und Halbach-Stiftung* is gratefully acknowledged.

Experimental

All reactions with ylides and with selenium-organic compounds were carried out in an inert atmosphere (argon) by using Schlenk-type glassware or in a glove box. Solvents were dried and distilled under argon prior to use. – NMR: Bruker AC 200 P (200 MHz, ^1H; 50 MHz ^{13}C) or WM 300 (300 MHz ^1H, 75 MHz ^{13}C). – IR: Nicolet 5 DXC FT. – Melting points (uncorrected): Büchi SMP 20 or DuPont DSC 910. – Elemental analyses: Foss-Heraeus CHN-Rapid elemental analyser. – The diarylcarbinol **2e** was used as purchased. Compounds **2c** and **2g** were prepared according to literature procedures[22]. The diarylmethyl halides **3a**, **3d**, **3h** (all X = Br) and **3f** (X = Cl) were used as available commercially. The compounds **3c**, **3e**, and **3g** were synthesized as described[23]. The phosphonium salts **4c**, **4d**, **4e**, and the ylides **5d** and **5e** were prepared according to literature procedures[15,24,25].

[Bis(4-methoxyphenyl)methyl]triphenylphosphonium Bromide (**4a**): To a solution of 10.0 g (40.8 mmol) of bis(4-methoxyphenyl)-methanol in 150 ml of dichloromethane was added at room temp. during 30 min 14.1 g (40.8 mmol) of triphenylphosphonium bromide in several portions. The mixture was stirred for 1 h and then the solvent was distilled off. The product was washed with hot ether to give 22.3 g (96%) of **4a**, m.p. (DSC) 180°C. – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1}, 2875, 1605, 1507, 1437, 1396, 1262, 1026. – ^1H NMR ($CDCl_3$): δ = 7.70–7.25 (m, 23H, arom. H), 6.58 (d, $^2J_{PH}$ = 8.5 Hz, 1H, C*H*PPh_3), 3.58 (s, 6H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 134.3 (J_{CP} = 3 Hz), 134.6 (J_{CP} = 9 Hz), 129.5 (J_{CP} = 12 Hz), 118.1 (J_{CP} = 82 Hz, Ph), 131.7 (J_{CP} = 7 Hz), 159.1 (J_{CP} = 2.4 Hz), 124.7, 113.8 (H_3CO–C_6H_4), 54.8 (OCH_3), 44.1 (J_{CP} = 42 Hz, *C*HPPh$_3$). – ^{31}P NMR ($CDCl_3$): δ = 21.7. – $C_{33}H_{30}BrO_2P$ (569.5): calcd. C 69.60, H 5.31; found C 68.92, H 5.74.

[Bis(4-fluorophenyl)methyl]triphenylphosphonium Chloride (**4f**): A glass tube was charged with a mixture of 21.4 g (89.7 mmol) of bis(4-fluorophenyl)methyl chloride and 25.0 g (95.3 mmol) of triphenylphosphane and then flame-sealed. The reaction mixture was then kept at 170°C for 6 h. The tube was opened. The colorless crystalline product was powdered and washed with two 200-ml portions of hot toluene, then with 150 ml of ether and dried in vacuo to give 35.6 g (85%) of **4f**, m.p. (DSC) 235.4°C. – IR (KBr): $\tilde{\nu}$ = 3003 cm^{-1}, 2806, 1600, 1500, 1438, 1229, 1161, 1108, 879, 830. – ^1H NMR ($CDCl_3$): δ = 8.70 (d, $^2J_{HP}$ = 18 Hz), 7.85–7.45 and 6.82 (m, 23H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 134.7 (J_{CP} = 9 Hz), 134.6 (J_{CP} = 3 Hz), 129.7 (J_{CP} = 12.5 Hz), 118.0 (J_{CP} = 82 Hz, PPh_3), 162.3 (J_{CF} = 249, J_{CP} = 2 Hz), 132.7 (J_{CF} = 8, J_{CP} = 9 Hz), 129.2 (J_{CF} = 3.5, J_{CP} = 4 Hz), 115.5 (J_{CF} = 22 Hz, FC_6H_4), 42.2 (J_{CP} = 43 Hz, *C*HPPh$_3$). – ^{31}P NMR ($CDCl_3$): δ = 22.8. – $C_{31}H_{24}ClF_2P$ (501.0): calcd. C 74.33, H 4.83; found C 74.30, H 4.86.

{Bis[3-(trifluoromethyl)phenyl]methyl}triphenylphosphonium Bromide (**4g**): Analogously as described above 8.45 g (22.0 mmol) of bis[3-(trifluoromethyl)phenyl]methyl bromide (**3g**) and 6.90 g (26.3 mmol) of triphenylphosphane were allowed to react in a sealed ampoule at 130°C for 16 h to give 12.0 g (85%) of **4g** as a white crystalline solid, m.p. (DSC) 230°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 2776, 1587, 1476, 1327, 1126, 1079, 916, 743. – ^1H NMR ($CDCl_3$): δ = 8.92 (d, $^2J_{HP}$ = 18 Hz, 1H, C*H*PPh_3), 8.42 and 7.90–7.40 (m, 23H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 135.1 (J_{CP} = 2.5 Hz), 134.9 (J_{CP} = 9 Hz), 130.1 (J_{CP} = 13 Hz), 119.1 (J_{CP} = 83 Hz, PPh_3), 135.6 (J_{CP} = 7.5 Hz), 134.0 (J_{CP} = 4 Hz), 130.7 (J_{CF} = 33 Hz), 130.0, 126.5 (J_{CF} = 4.5 Hz), 125.5 ($CF_3C_6H_4$), 123.3 (J_{CF} = 272 Hz,

CF_3), 44.7 (J_{CP} = 43 Hz, *C*HPPh$_3$). – ^{31}P NMR ($CDCl_3$): δ = 23.5. – $C_{33}H_{24}BrF_6P$ (565.5): calcd. C 61.51, H 3.75; found C 60.88, H 3.72.

[(4-Chlorophenyl)phenylmethyl]triphenylphosphonium Chloride (**4h**): Analogously as described above 24.3 g (108.0 mmol) of (4-chlorophenyl)phenylmethyl chloride (**3h**) and 25.0 g (95.3 mmol) of triphenylphosphane were allowed to react in a sealed glass tube at 160°C for 6 h to yield 39.4 g (88%) of **4h** as a white solid, m.p. (DSC) 238°C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2993, 2769, 1588, 1487, 1441, 1411, 1108, 1014, 817. – ^{1}H NMR ($CDCl_3$): δ = 8.70 (d, $^2J_{HP}$ = 18 Hz, 1H, C*H*PPh$_3$), 7.85–7.50 and 7.18 (m, 24H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 134.8 (J_{CP} = 9 Hz), 132.0 (J_{CP} = 2 Hz), 129.7 (J_{CP} = 12 Hz), 118.1 (J_{CP} = 82 Hz, PPh$_3$), 134.6 (J_{CP} = 2 Hz), 133.0 (J_{CP} = 4 Hz), 132.3 (J_{CP} = 7 Hz), 128.7 (Ph), 134.3 (J_{CP} = 3.5 Hz), 130.8 (J_{CP} = 7 Hz), 128.8, 128.5 (J_{CP} = 2 Hz, ClC_6H_4), 43.9 (J_{CP} = 42 Hz, *C*PPh$_3$). – ^{31}P NMR ($CDCl_3$): δ = 22.7. – $C_{31}H_{25}Cl_2P$ (499.4): calcd. C 74.55, H 5.05; found C 74.33, H 5.02.

[Bis(4-methoxyphenyl)methylene]triphenylphosphorane (**5a**): The alkylidenephosphoranes **5** used in this study were all prepared by a synthetic procedure similar to the one developed by Bestmann et al.[15] The phosphonium salt **4a** (11.5 g, 20.0 mmol) was dissolved in 300 ml of toluene/tetrahydrofuran (2:1). Sodium amide (0.79 g, 20.0 mmol) was added and the mixture stirred at ambient temp. for 15 h. Argon was passed through the solution for 10 min. The precipitated sodium halide was filtered off and washed with toluene. The combined organic solution was stripped in vacuo to give the ylide **5a** as a light red solid, yield 8.8 g (85%), m.p. (DSC) 102°C. – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2834, 1601, 1498, 1436, 1236, 1179, 1033, 994, 815. – ^{1}H NMR ([D$_6$]benzene): δ = 7.65, 6.98, 6.67 (m, 23H, arom. H), 3.33 (s, 6H, OCH_3). – ^{13}C NMR ([D$_6$]benzene): δ = 134.4 (J_{CP} = 9.5 Hz), 131.9 (J_{CP} = 58 Hz), 131.3, 128.4 (J_{CP} = 12 Hz, PPh$_3$), 154.6, 139.0 (J_{CP} = 13 Hz), 130.9 (J_{CP} = 7 Hz), 114.2 (CH_3O–C_6H_4), 54.9 (OCH_3), 44.1 (J_{CP} = 41.5 Hz, *C*PPh$_3$). – ^{31}P NMR ([D$_6$]benzene): δ = 6.0. – $C_{33}H_{29}O_2P$ (488.6): calcd. C 81.13, H 5.98; found C 80.12, H 5.94.

[(4-Methylphenyl)phenylmethylene]triphenylphosphorane (**5c**): Deprotonation of 4.0 g (8.4 mmol) of the phosphonium salt **4c** was carried out as described above by the reaction with 0.3 g (8.4 mmol) of sodium amide in 100 ml of toluene/tetrahydrofuran (2:1) at room temp. for 24 h. Workup of the reaction mixture as outlined above yielded 3.1 g (83%) of **5c** (orange-colored crystals), m.p. (DSC) 109°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3012 cm^{-1}, 1584, 1482, 1436, 1214, 1093, 997, 751, 710. – ^{1}H NMR ([D$_6$]benzene): δ = 7.60, 7.15, 6.94 (m, 24H, arom. H), 2.12 (s, 3H, CH_3). – ^{13}C NMR ([D$_6$]benzene): δ = 134.1 (J_{CP} = 9.5 Hz), 130.6 (J_{CP} = 61 Hz), 128.9 (J_{CP} = 5 Hz), 128.2 (J_{CP} = 12 Hz, PPh$_3$), 146.7 (J_{CP} = 13 Hz), 132.7 (J_{CP} = 6 Hz), 128.6, 117.9 (ClC_6H_4), 141.3 (J_{CP} = 13 Hz), 130.9, 126.9 (J_{CP} = 5 Hz), 117.9 (Ph), 41.1 (J_{CP} = 132 Hz), 20.7 (s, CH_3). – ^{31}P NMR ([D$_6$]benzene): δ = 7.2. – $C_{32}H_{27}P$ (442.5): calcd. 86.85, H 6.15; found C 85.41, H 6.16.

[Bis(4-fluorophenyl)methylene]triphenylphosphorane (**5f**): Analogously as described above 14.7 g (29.3 mmol) of the phosphonium salt **4f** was dissolved in 300 ml of toluene/tetrahydrofuran (2:1) and deprotonated with 1.2 g (31.3 mmol) of sodium amide (ambient temp., 36 h). Workup of the reaction mixture as described above gave 12.7 g (91%) of the ylide **5f** as a light red solid, m.p. 190°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 1595, 1494, 1293, 1209, 1092, 1013, 814, 692. – ^{1}H NMR ([D$_6$]benzene): δ = 7.48 (dd, $^3J_{HH}$ = 8, $^3J_{HF}$ = 12 Hz, 4H) and 6.69 (dd, $^3J_{HH}$ = 8, $^4J_{HF}$ = 8.5 Hz, 4H, FC_6H_4), 6.90 (m, 15H, Ph_3P). – ^{13}C NMR ([D$_6$]benzene): δ = 134.2 (J_{CP} = 10 Hz), 131.5 (J_{CP} = 3 Hz), 130.2 (J_{CP} = 66 Hz), 128.5 (J_{CP} = 12 Hz, PPh$_3$), 158.5 (J_{CF} = 232 Hz), 141.8 (J_{CP} = 13 Hz), 132.3 (J_{CF} = 10 Hz), 115.4 (J_{CF} = 24 Hz, FC_6H_4), 40.2 (J_{CP} = 118 Hz, *C*PPh$_3$). – ^{31}P NMR ([D$_6$]benzene): δ = 7.5. – $C_{31}H_{23}F_2P$ (464.5): calcd. C 80.16, H 4.99; found C 80.72, H 5.45.

{Bis[3-(fluoromethyl)phenyl]methylene}triphenylphosphorane (**5g**): As described above 12.0 g (18.9 mmol) of the phosphonium salt **4g** in 250 ml of toluene/tetrahydrofuran (2:1) was deprotonated with 0.9 g (22.5 mmol) of sodium amide (room temp., 15 h) to give 8.4 g (79%) of the ylide **5g**, yellow solid, m.p. (DSC) 112°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 1596, 1436, 1340, 1157, 1095, 1021, 912, 776. – ^{1}H NMR ([D$_6$]benzene): δ = 7.39–7.28 (m, 8H), 6.93–6.75 (m, 15H, arom. H). – ^{13}C NMR ([D$_6$]benzene): δ = 134.1 (J_{CP} = 9.5 Hz), 132.0 (J_{CP} = 2 Hz), 129.3 ($^1J_{CP}$ not determined), 128.9 (J_{CP} = 12 Hz, PPh$_3$), 145.9 (J_{CP} = 13 Hz), 132.6 (J_{PC} = 7 Hz), 130.7 (J_{CF} = 33 Hz), 128.7, 125.3, 116.7 (J_{CP} = 4 Hz, $CF_3C_6H_4$), 126.8 (J_{CF} = 260 Hz, CF_3), 44.6 (J_{CP} = 131 Hz, *C*PPh$_3$). – ^{31}P NMR ([D$_6$]benzene): δ = 10.1. – $C_{33}H_{23}F_6P$ (564.1): calcd. C 70.21, H 4.11; found C 69.94, H 4.30.

[(4-Chlorophenyl)phenylmethylene]triphenylphosphorane (**5h**): As described above in detail 10.0 g (20.2 mmol) of the phosphonium salt **4h** was treated with 0.8 g (23.0 mmol) of sodium amide in 250 ml of toluene/tetrahydrofuran (2:1) to give 6.2 g (67%) of the orange-colored ylide **5h**, m.p. (DSC) 141°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1}, 1579, 1481, 1312, 1213, 1091, 993, 811. – ^{1}H NMR ([D$_6$]benzene): δ = 7.49 (m, 6H), 6.85 (m, 18H, arom. H). – ^{13}C NMR ([D$_6$]benzene): δ = 134.3 (J_{CP} = 9 Hz), 131.5 (J_{CP} = 3 Hz), 129.5 (J_{CP} = 56 Hz), 128.7 (J_{CP} = 12 Hz, PPh$_3$), 144.7 (J_{CP} = 13 Hz), 132.3 (J_{CP} = 9 Hz), 131.6, 124.0 (Ph), 145.1 (J_{CP} = 14 Hz), 129.1 (J_{CP} = 8 Hz), 128.4, 121.4 (ClC_6H_4), 41.6 (J_{CP} = 87 Hz, *C*PPh$_3$). – ^{31}P NMR ([D$_6$]benzene): δ = 8.0. – $C_{31}H_{24}ClP$ (462.9): calcd. C 80.43, H 5.22; found C 80.63, H 5.61.

3,6-Dihydro-2,2-bis(4-methoxyphenyl)-4,5-dimethyl-2H-selenapyran (**7a**): A sample of 0.5 g (1.0 mmol) of the ylide **5a** was dissolved in 50 ml of toluene. Selenium (0.16 g, 2.0 mmol) and 0.58 g (7.1 mmol) of 2,3-dimethylbutadiene were added. The mixture was stirred at 75°C for 8 h. Remaining selenium was filtered off. The solvent was removed in vacuo, the remaining solid taken up in pentane and the solution filtered. The filtrate was concentrated in vacuo and the residue chromatographed with pentane on silica gel to yield 0.24 g (63%) of **7a** as a colorless oil. – IR (film): $\tilde{\nu}$ = 3024 cm^{-1}, 2963, 2906, 1605, 1504, 1442, 1260, 1093, 1028, 801. – ^{1}H NMR ([D$_6$]benzene): δ = 7.43, 6.73 (AA'XX', ^3J = 9 Hz, 8H, $CH_3OC_6H_4$), 3.30 (s, 6H, OCH_3), 2.96, 2.79 (s, 2H, each, 3-, 6-H), 1.56, 1.47 (s, 3H each, 4-CH_3, 5-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 157.9, 139.2, 129.2 ($^1J_{CH}$ = 156 Hz), 113.1 ($^1J_{CH}$ = 159 Hz, $CH_3OC_6H_4$), 128.6, 124.3 (C-4, -5), 55.1 ($^1J_{CH}$ = 143 Hz, OCH_3), 50.5 (C-2), 48.0 ($^1J_{CH}$ = 130 Hz, C-3), 24.7 ($^1J_{CH}$ not determined, C-6), 20.7 ($^1J_{CH}$ = 125 Hz) and 20.0 ($^1J_{CH}$ = 126 Hz, 4-CH_3 and 5-CH_3). – $C_{21}H_{18}O_2Se$ (387.4): calcd. C 65.11, H 6.24; found C 64.91, H 5.88.

3,6-Dihydro-4,5-dimethyl-2-(4-methylphenyl)-2-phenyl-2H-selenapyran (**7c**): Analogously as described above 0.3 g (0.7 mmol) of the ylide **5c** was treated with 0.1 g (1.3 mmol) of selenium in 35 ml of toluene in the presence of 0.2 g (3.0 mmol) of 2,3-dimethylbutadiene (75°C, 12 h). Workup of the reaction mixture as described above yielded 0.17 g (86%) of **7c** as a colorless amorphous solid, m.p. (DSC) 81°C. – IR (KBr): $\tilde{\nu}$ = 3027 cm^{-1}, 2963, 2858, 1510, 1493, 1444, 1261, 1093, 790. – ^{1}H NMR ($CDCl_3$): δ = 7.37–7.04 (m, 9H, arom. H), 2.94 and 2.87 (s, each 2H, 3-, 6-H), 2.31 (s, 3H, $C_6H_4CH_3$), 1.73 (br. s, 6H, 4-CH_3, 5-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 147.1, 144.0, 135.9, 128.6, 128.2, 128.0, 127.8, 126.3 (Ph and Me–C_6H_4), 128.1 and 124.3 (C-5, -4), 51.5 (C-2), 47.6 (C-3), 24.6 (C-6), 20.9, 20.1, and 20.0 (4-CH_3, 5-CH_3, and $C_6H_4CH_3$). – $C_{20}H_{22}Se$ (341.3): calcd. C 70.37, H 6.50; found C 70.04, H 6.85.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-4,5-dimethyl-2H-selenapyran (**7e**): The ylide **5e** (2.4 g, 4.8 mmol) was treated with 0.77 g (9.6 mmol) of selenium and 2.9 g (35.2 mmol) of 2,3-dimethylbutadiene in 200 ml toluene at 75°C for 9 h. Workup of the reaction mixture as described above gave 1.2 g (64%) of **7e** as a slightly yellow oil. – IR (film): $\tilde{\nu}$ = 3027 cm^{-1}, 2857, 1488, 1093, 822. – ^1H NMR ($CDCl_3$): δ = 7.18 (m, 8H, ClC_6H_4), 2.81 (s, 4H, 3-, 6-H), 1.68, 1.66 (s, 3H each, 4-CH_3, 5-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 145.0, 129.5 ($^1J_{CH}$ = 160 Hz), 128.1, 127.9 ($^1J_{CH}$ = 165 Hz, ClC_6H_4), 132.3 and 124.7 (C-5, -4), 50.4 (C-2), 47.3 ($^1J_{CH}$ = 128 Hz, C-3), 24.7 ($^1J_{CH}$ = 140 Hz, C-6), 20.6 ($^1J_{CH}$ = 126 Hz) and 19.7 ($^1J_{CH}$ = 127 Hz, 4-CH_3, 5-CH_3). – $C_{19}H_{18}Cl_2Se$ (396.2): calcd. C 57.56, H 4.58; found C 57.86, H 4.66.

2,2-Bis(4-fluorophenyl)-3,6-dihydro-4,5-dimethyl-2H-selenapyran (**7f**): 1.67 g (3.5 mmol) of the ylide **5f** was allowed to react with 0.56 g (7.1 mmol) of selenium and 2.05 g (2.5 mmol) of 2,3-dimethylbutadiene in 150 ml of toluene at 75°C for 12 h to give 0.95 g (75%) of **7f** as a colorless oil. – IR (film): $\tilde{\nu}$ = 3027 cm^{-1}, 2923, 1601, 1506, 1439, 1161, 738. – ^1H NMR ($CDCl_3$): δ = 7.25 (m, $^3J_{HH}$ = 9, $^4J_{HF}$ = 5 Hz, 4H), 6.89 (m, $^3J_{HH}$ = 9, $^3J_{HF}$ = 9 Hz, 4H, FC_6H_4), 2.85 (s, 4H, 3-, 6-H), 1.69 (s, 6H, 4-CH_3, 5-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 161.2 (J_{CF} = 247 Hz), 142.5, 128.6 ($^1J_{CH}$ = 160, J_{CF} = 7 Hz), 114.7 ($^1J_{CH}$ = 168, J_{CF} = 22 Hz, FC_6H_4), 128.3 and 124.6 (C-5, -4), 50.3 (C-2), 47.8 ($^1J_{CH}$ = 125 Hz, C-3), 24.8 ($^1J_{CH}$ = 142 Hz, C-6), 20.7 ($^1J_{CH}$ = 126 Hz) and 19.9 ($^1J_{CH}$ = 127 Hz, 4-CH_3 and 5-CH_3). – $C_{19}H_{18}F_2Se$ (363.3): calcd. C 62.81, H 4.99; found C 62.59, H 4.71.

3,6-Dihydro-4,5-dimethyl-2,2-bis[3-(trifluoromethyl)phenyl]-2H-selenapyran (**7g**): 0.52 g (0.9 mmol) of the ylide **5g** was allowed to react with 0.15 g (1.9 mmol) of selenium and 0.53 g (6.5 mmol) of 2,3-dimethylbutadiene in 50 ml of toluene/tetrahydrofuran (1:1) at 75°C for 12 h. The reaction mixture was worked up as described above to give 0.31 g (67%) of **7g** as a colorless solid, m.p. (DSC) 55°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2963, 2891, 1610, 1439, 1328, 1261, 1116, 1073, 1020, 801. – ^1H NMR ([D_6]benzene): δ = 7.82 (s, 2H), 7.22 (m, 4H), 6.84 (m, 2H, $CF_3C_6H_4$), 2.64, 2.57 (s, 2H each, 3-, 6-H), 1.37 and 1.35 (s, each, 3H, 4-CH_3, 5-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 147.2, 131.7, 130.4 (J_{CF} = 33 Hz), 128.6, 124.8 (J_{CF} = 3.5 Hz), 123.7 (J_{CF} = 3.5 Hz, $CF_3C_6H_4$), 128.1, 125.5 (C-5, -4), 124.0 (J_{CF} = 272 Hz, CF_3), 51.2 (C-2), 47.1 (C-3), 24.9 (C-6), 20.6 and 19.7 (4-CH_3, 5-CH_3). – $C_{21}H_{18}F_6Se$ (463.3): calcd. C 54.43, H 3.92; found C 55.05, H 3.82.

2-(4-Chlorophenyl)-3,6-dihydro-4,5-dimethyl-2-phenyl-2H-selenapyran (**7h**): 0.70 g (1.6 mmol) of the ylide **5h** was treated with 0.26 g (3.2 mmol) of selenium and 0.66 g (8.0 mmol) of 2,3-dimethylbutadiene in 75 ml of toluene at 75°C for 48 h. Workup of the reaction mixture as described above yielded 0.36 g (73%) of **7h** as a colorless solid, m.p. (DSC) 90°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2919, 1598, 1490, 1444, 1263, 1093, 1013, 740. – ^1H NMR ($CDCl_3$): δ = 7.22 (m, 9H, arom. H), 2.91, 2.86 (s, each 2H, 3-, 6-H), 1.71 (br. s, 6H, 4-CH_3, 5-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 146.7, 139.5, 132.0, 129.8, 128.1, 128.0, 127.9, 125.6 (arom. C), 128.4, 124.6 (C-5, -4), 51.1 (C-2), 47.4 (C-3), 24.6 (C-6), 20.7 and 20.0 (4-CH_3, 5-CH_3). – $C_{19}H_{20}ClSe$ (362.7): calcd. C 62.92, H 5.56; found C 62.39, H 5.65.

3,6-Dihydro-2-(4-methylphenyl)-2-phenyl-2H-selenapyran (**8c**): 0.5 g (1.1 mmol) of the ylide **5c** was allowed to react with 0.15 g (1.9 mmol) of selenium at 85°C for 4 h in 50 ml of toluene. The mixture was cooled to −78°C, and 0.25 g (5.5 mmol) of 1,3-butadiene was condensed into the reaction mixture. The green mixture was then allowed to warm to room temp. during 1 h with stirring. The reaction was brought to completion by keeping the mixture at 50°C until it became almost colorless. Excess selenium was filtered off. The solvent was removed from the clear filtrate in vacuo. The residue was taken up in ether and the solution filtered from a triphenylphosphane selenide precipitate. The filtrate was concentrated in vacuo, the residue taken up in pentane and the solution filtered through a short silica gel column. The solvent was removed from the filtrate to give 0.22 g (73%) of **8c** as a colorless solid, m.p. (DSC) 60°C. – IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1}, 2904, 1550, 1260, 1011. – ^1H NMR ($CDCl_3$): δ = 7.42–6.85 (m, 9H, arom. H), 5.89, 5.81 (m, 1H each, 5-, 4-H), 3.04, 2.89 (m, 2H each, 3-, 6-H), 2.28 (s, $C_6H_4CH_3$). – ^{13}C NMR ($CDCl_3$): δ = 146.6, 143.5, 136.1, 128.7, 128.3, 128.1, 128.0, 126.4 (arom. C), 129.9 and 124.6 (C-5, -4), 50.2 (C-2), 40.2 (C-3), 20.9 ($C_6H_4CH_3$), 19.3 (C-6). – $C_{18}H_{18}Se$ (313.3): calcd. C 69.01, H 5.79; found C 69.18, H 5.75.

3,6-Dihydro-2,2-diphenyl-2H-selenapyran (**8d**): 1.0 g (diphenylmethylene)triphenylphosphorane (**5d**) was allowed to react with 0.37 g (4.6 mmol) of selenium in 100 ml of toluene at 85°C for 3 h. The resulting green reaction mixture was treated with 0.6 g (11.5 mmol) of 1,3-butadiene and worked up as described above to yield 0.43 g (63%) of **8d** as a colorless solid, m.p. (DSC) 86°C. – IR (KBr): $\tilde{\nu}$ = 3017 cm^{-1}, 2886, 1597, 1490, 1406, 1262, 1081, 1035, 742, 698. – ^1H NMR ($CDCl_3$): δ = 7.38 (m, 4H), 7.20 (m, 6H, Ph), 5.91, 5.82 (m, 1H each, 5-, 4-H), 3.05, 2.91 (m, 2H each, 3-, 6-H). – ^{13}C NMR ([D_6]benzene): δ = 146.4, 128.3, 127.9, 126.5 (Ph), 129.8, 124.8 (C-5, -4), 50.6 (C-2), 40.4 (C-3), 19.2 (C-6). – $C_{17}H_{16}Se$ (299.2): calcd. C 68.23, H 5.39; found C 67.85, H 5.43.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-2H-selenapyran (**8e**): From 1.0 g (2.0 mmol) of the ylide **5e** and 0.32 g (4.1 mmol) of selenium in 100 ml of toluene was obtained a green reaction mixture at 60°C after 6 h, which was treated with 0.56 g (10.0 mmol) of butadiene and worked up analogously as described above to yield 0.52 g (76%) of **8e** as a yellow oil. – IR (film): $\tilde{\nu}$ = 3026 cm^{-1}, 2904, 1661, 1491, 1261, 1092, 1014, 822, 732. – ^1H NMR ($CDCl_3$): δ = 7.12, 7.01 (AA'XX', $^3J_{HH}$ = 9 Hz, 8H, ClC_6H_4), 5.91, 5.85 (m, 1H each, 5-, 4-H), 3.03 and 2.94 (m, 2H each, 3-, 6-H). – ^{13}C NMR ([D_6]benzene): δ = 145.0, 132.8, 130.0, 128.4 (ClC_6H_4), 129.4, 124.8 (C-5, -4), 48.8 (C-2), 40.0 (C-3), 19.4 (C-6). – $C_{17}H_{14}Cl_2Se$ (368.2): calcd. C 55.46, H 3.83; found C 54.79, H 3.83.

2,2-Bis(4-fluorophenyl)-3,6-dihydro-2H-selenapyran (**8f**): 1.0 g (2.2 mmol) of the ylide **5f** was treated with 0.3 g (4.2 mmol) of selenium in 100 ml of toluene at 75°C for 3 h. Subsequent reaction with 0.56 g (10.5 mmol) of butadiene and workup of the reaction mixture as described above gave 0.46 g (66%) of **8f** as a yellow oil. – IR (film): $\tilde{\nu}$ = 3026 cm^{-1}, 2901, 1601, 1505, 1406, 1233, 1161, 832, 700. – ^1H NMR ($CDCl_3$): δ = 7.34 (dd, $^3J_{HH}$ = 9, $^4J_{HF}$ = 5 Hz, 4H, arom. H), 6.95 (dd, $^3J_{HH}$ = 9, $^3J_{HF}$ = 9 Hz, 4H, arom. H), 5.90, 5.85 (m, 1H each, 5-, 4-H), 3.02, 2.94 (m, 2H each, 3-, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 161.7 (J_{CF} = 8 Hz), 114.9 (J_{CF} = 22 Hz, FC_6H_4), 129.5, 124.7 (C-5, -4), 48.9 (C-2), 40.5 (C-3), 19.4 (C-6). – $C_{17}H_{14}F_2Se$ (335.3): calcd. C 60.91, H 4.21; found C 60.93, H 5.03.

2-(4-Chlorophenyl)-3,6-dihydro-2-phenyl-2H-selenapyran (**8h**): The reaction of 1.0 g (2.2 mmol) of the ylide **5h** with 0.33 g (4.2 mmol) of selenium in 100 ml of toluene at 80°C for 8 h gave a green mixture. Subsequent reaction with 0.5 g (10.5 mmol) of butadiene and workup of the mixture as described above yielded 0.5 g (69%) of **8h** as a slightly yellow oil which was contaminated with a small amount of 1,2-bis(4-chlorophenyl)-1,2-diphenylethene. **8h**: IR (film): $\tilde{\nu}$ = 3025 cm^{-1}, 2964, 1490, 1261, 1093, 1014, 898, 798. – ^1H NMR ($CDCl_3$): δ = 7.39–6.93 (m, 9H, arom. H), 5.52, 5.41 (m, 1H each, 5-, 4-H), 3.04, 2.89 (m, 2H each, 3-, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 144.6, 141.1, 132.9, 132.5, 132.4, 129.6, 128.3, 128.2 (arom. C), 129.2, 124.7 (C-5, -4), 48.8 (C-2), 40.0 (C-3), 19.3 (C-6). – $C_{17}H_{15}ClSe$ (333.7): calcd. C 61.19, H 4.53; found C 62.01, H 5.32.

3,6-Dihydro-4,5-dimethoxy-2,2-diphenyl-2H-selenapyran (**9**). – a) *From (diphenylmethylene)triphenylphosphorane* (**4d**): A mixture of 1.0 g (2.3 mmol) of the ylide **4d** and 0.37 g (4.6 mmol) of selenium in 100 ml of toluene was allowed to react at 85°C for 2 h. Remaining selenium was filtered off, and the resulting green solution was charged with 1.9 g (16.6 mmol) of 2,3-dimethoxybutadiene. The solution was stirred at room temp. for 24 h. The solvent was removed in vacuo from the resulting almost colorless solution. The residue was taken up in 50 ml of ether and the solution filtered from a precipitate. The filtrate was concentrated to about one half of its original volume and filtered again. The product crystallized from the filtrate at −30°C and was collected by filtration; yield of **9**: 0.57 g (70%), m.p. 93−94°C. – b) *From 2,2,4,4-tetraphenyl-1,3-diselenacyclobutane:* a sample (150 mg, 0.30 mmol) of freshly sublimed **1d**-dimer was dissolved in 20 ml of toluene. Then 2,3-dimethoxybutadiene (470 mg, 4.0 mmol) was added to the solution and the reaction mixture stirred at ambient temp. for 6 h. The solvent was then removed in vacuo. The residue was taken up in 10 ml of ether, and the product was crystallized at −30°C to give crystals of **9** that were suited for the X-ray crystal structure analysis. The product was collected by filtration and the filtrate concentrated in vacuo to ca. 1/3 of its volume to give an additional amount of **9** at −30°C; combined yield 95 mg (88%). – IR (KBr): $\tilde{\nu} = 3048$ cm^{-1}, 2983, 1694, 1443, 1247, 1168, 1099, 984, 732, 698. – MS (EI), *m/z* (%): 360 (7) [M$^+$], 246 (100) [M$^+$ − $C_6H_{10}O_2$], 165 (58), 77 (13). – ^{1}H NMR ($CDCl_3$): δ = 7.09−7.33 (m, 10H, Ph), 3.38 and 3.55 (s, 3H each, OCH_3), 3.21, 2.82 (m, 2H each, 3-, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 145.2, 131.3 ($^1J_{CH}$ = 170 Hz), 128.0 ($^1J_{CH}$ = 153 Hz), 126.7 ($^1J_{CH}$ = 161 Hz, Ph), 142.0, 138.5 (C-4, -5), 58.1 ($^1J_{CH}$ = 144 Hz), 57.6 ($^1J_{CH}$ = 144 Hz, 4-OCH_3, 5-OCH_3), 51.0 (C-2), 43.7 ($^1J_{CH}$ = 129 Hz, C-3), 17.5 ($^1J_{CH}$ = 142 Hz, C-6). – $C_{19}H_{20}O_2Se$ (359.3): calcd. C 63.42, H 5.60; found C 63.51, H 5.59.

X-Ray Crystal Structure Determination of **9**[26]: Molecular formula $C_{19}H_{20}O_2Se$, molecular weight 359.3 g · mol^{-1}, crystal colorless, crystal size 0.22 × 0.32 × 0.29 mm, $a = 10.891(1)$, $b = 10.154(1)$, $c = 15.319(2)$ Å, $\beta = 96.03(1)°$, $V = 1684.7$ Å^3, $d_{cal} = 1.42$ g · cm^{-3}, $\mu = 22.08$ cm^{-1}, Mo-K_α radiation, $\lambda = 0.71069$ Å, $F(000) = 736$ e, $Z = 4$, crystal system monoclinic, space group $P2_1/n$ (No. 14), Enraf-Nonius CAD4 diffractomcter, scan mode ω-2Θ, $[(\sin\Theta)/\lambda] = 0.65$ Å^{-1}, 7657 measured reflections ($\pm h$, $\pm k$, $+l$), 3829 independent reflections, 2255 observed reflections [$I > 2\sigma(I)$] for 279 refined parameters, structure solved by direct methods, H atom positions found and refined in the final least-squares refinement, $R = 0.036$, $R_w = 0.027$, residual electron density 0.51 eÅ^{-3}.

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