Oxygen–Selenium Exchange using Phenylselenophosphonic Dichloride [PhP(Se)Cl_2]: Conversion of C=O into C=Se

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Phenylselenophosphonic dichloride brings about preparatively useful oxygen–selenium exchange reactions in conjugated carbonyl and masked carbonyl compounds, thus enabling tertiary selenoamides, indolizine-3-selenoaldehydes, 1,2-dithiol-3-selones, 1,6aλ^4-dithia-6-selenapentalenes, and 6aλ^4-thia-6-selena-1,2-diazapentalenes to be prepared.

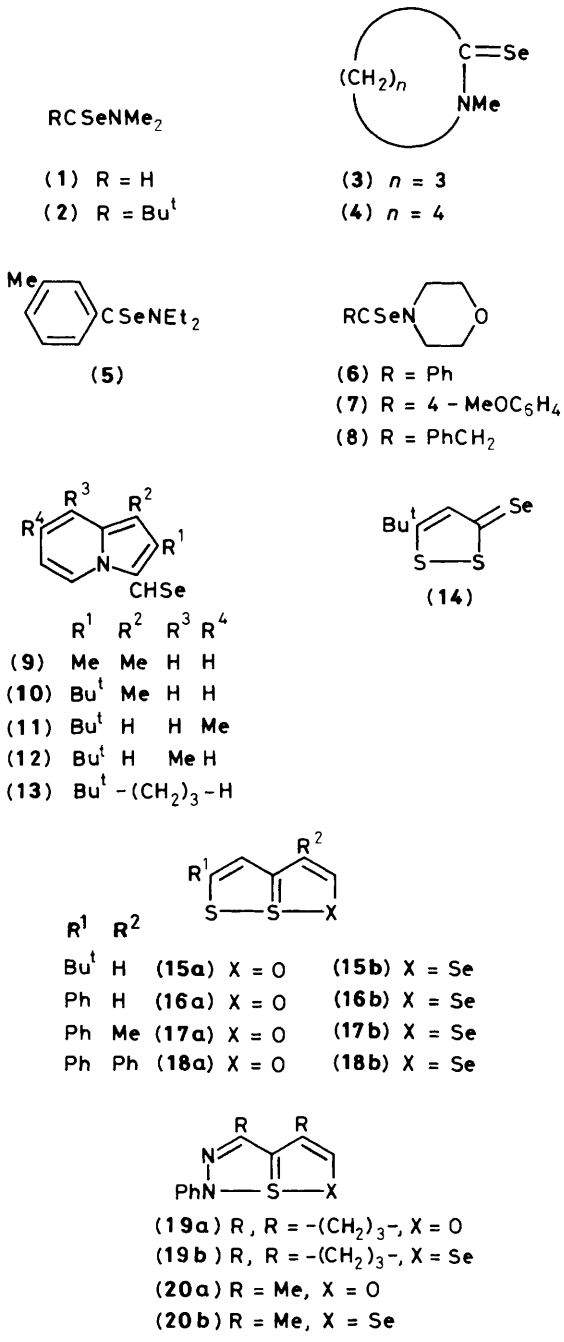
Few good methods exist for forming the selenocarbonyl group.[1] Tetraphosphorus decaselenide, the reagent most commonly used to effect the direct conversion of C=O into C=Se, is virtually insoluble in organic media. Consequently its reactions are heterogeneous, inefficient, often involve high temperatures, and give poor yields of product. In a search for more efficient reagents for carrying out oxygen–selenium exchange, we have found that phenylselenophosphonic dichloride[2] reacts with various types of conjugated carbonyl and masked carbonyl compounds under mild conditions to give the corresponding selenocarbonyl compound, in most cases in satisfactory to excellent yield.

Phenylselenophosphonic dichloride is soluble in a wide range of inert solvents, allowing the reactions to be carried out

Table 1. Preparation of selenoamides (**1**)—(**8**),[a] the indolizine-3-selenoaldehydes (**9**)—(**13**),[b] the 1,2-dithiol-3-selone (**14**),[c] and the selenapentalenes (**15b**)—(**20b**).[d]

Product[e]	Reaction time/h (min)	% Yield
(**1**)	3	84
(**2**)	8	13
(**3**)	4	96
(**4**)	4	54
(**5**)	4	61[f]
(**6**)	24	76
(**7**)	15	84
(**8**)	15	61
(**9**)	(10)	71
(**10**)	(10)	81
(**11**)	(10)	72
(**12**)	(10)	62[g]
(**13**)	(10)	67[h]
(**14**)	4	26[i]
(**15b**)	1	73[j]
(**16b**)	1.5	79[k]
(**17b**)	1.5	62[l]
(**18b**)	1.5	67
(**19b**)	0.5	79
(**20b**)	1	86

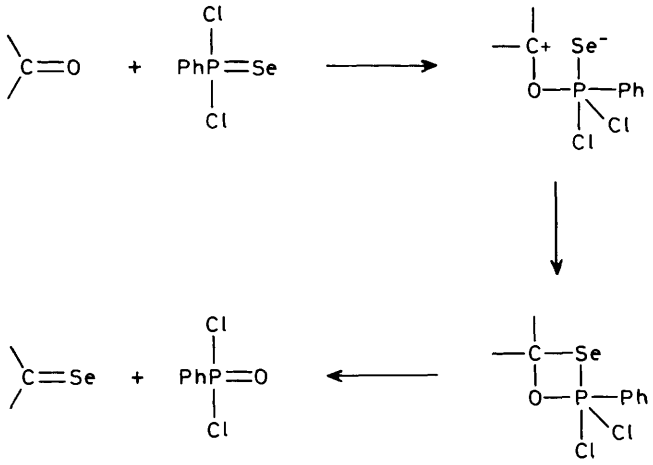
[a] The amide (10 mmol) was heated with a 2 M-solution of $PhP(Se)Cl_2$ in xylene (12.5 ml, 25 mmol) at 95—100 °C for the time specified. The cooled solution was diluted with benzene (100 ml), alumina (activity II—III, 70—230 mesh, 100 g) was added, and the resulting slurry was transferred to the top of a column of alumina (15 × 2.6 cm). Elution with hexane–benzene removed the xylene and subsequent elution with benzene–ether or ether gave the yellow selenoamide. [b] A 2 M solution of $PhP(Se)Cl_2$ in xylene (1.825 ml, 3.75 mmol) was added to a solution of the aldehyde (2.5 mmol) in dichloromethane (50 ml) at room temperature. After 10 min the solution was poured onto a column of alumina (activity II—III, 70—230 mesh, 20 × 2.6 cm). Elution with benzene followed by benzene–ether (9 : 1) gave green eluates which yielded the selenoaldehyde. [c] 5-t-Butyl-1,2-dithiol-3-one (5 mmol) and a 2 M-solution of $PhP(Se)Cl_2$ in xylene (50 ml) were dissolved in toluene (200 ml), and the resulting solution was boiled, cooled, and chromatographed on alumina. [d] A 2 M solution of $PhP(Se)Cl_2$ in xylene (1.25 ml, 2.5 mmol) was added to a solution of triethylamine (10 mmol) and the oxadithiapentalene or oxathiadiazapentalene (1 mmol) in dichloromethane (10 ml) at room temperature. Chromatography gave the purple selenapentalene. [e] Physical data of known compounds were in accord with previously recorded values (refs. 3—7). Satisfactory elemental analyses were obtained for all new compounds, and ^1H and ^{13}C n.m.r. data were in agreement with their structures. [f] M.p. 87—88 °C. [g] M.p. 169.5—170.5 °C. [h] M.p. 186.5—188 °C. [i] M.p. 130—131 °C. [j] M.p. 71—72 °C. [k] M.p. 144—144.5 °C. [l] M.p. 117—117.5 °C.



under homogeneous conditions. It is readily prepared by the reaction of phenyldichlorophosphine with a 20% excess of powdered selenium at 170—175 °C for 40 min in an inert atmosphere (*cf.* ref. 2). The resulting $PhP(Se)Cl_2$, which is formed quantitatively, is dissolved in a suitable inert solvent (dichloromethane, benzene, toluene), the solution is filtered to remove the excess of selenium, and sufficient additional solvent is added to give a solution of known concentration. In the work described below and summarised in Table 1, we used a 2 M-solution in xylene.

The tertiary selenoamides (**1**)—(**8**) were obtained by heating the corresponding amides with an excess of the reagent at 95—100 °C for several hours. Yields in all cases were superior to those obtained by previously reported methods [(**1**) and (**6**)—(**8**), ref. 3; (**2**)—(**4**), ref. 4]. The selenoaldehydes (**9**)—(**13**) were formed rapidly by reaction of the corresponding aldehydes with $PhP(Se)Cl_2$ at room temperature. In a previously reported method,[5] indolizine-3-selenoaldehydes had been synthesised from indolizines in 28—46% yield by a modification of the Vilsmeier reaction. 5-t-Butyl-1,2-dithiol-3-one also reacted with $PhP(Se)Cl_2$, in boiling toluene, to give the corresponding selone (**14**), albeit in modest yield (26%).

In some reactions of $PhP(Se)Cl_2$, improved yields of products resulted from carrying out the reactions in the presence of triethylamine. The added base removes traces of hydrogen chloride formed by exposure of the reagent to atmospheric moisture, and thereby suppresses acid-catalysed side reactions. Thus the oxadithiapentalenes (**15a**)—(**18a**) and the oxathiadiazapentalenes (**19a**) and (**20a**), which are masked



Scheme 1

carbonyl compounds, reacted at room temperature with $PhP(Se)Cl_2$, best in the presence of triethylamine, to give the dithiaselenapentalenes (**15b**)—(**18b**) and the thiaselenadiazapentalenes (**19b**) and (**20b**), respectively, in good yield.

We propose that the oxygen–selenium exchange process takes place as depicted in Scheme 1. Advantages in the use of $PhP(Se)Cl_2$ are that the starting materials for its preparation are readily available and inexpensive, reaction takes place in a homogeneous medium under mild conditions, and $PhP(O)Cl_2$ and unreacted $PhP(Se)Cl_2$ are removed easily by chromatography on alumina.

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