α-Chlorination and Carbonylolefination: Synthesis of Phenyl 1-Chloro-1-alken-1-yl Selenides (Chlorovinyl Phenyl Selenides)

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The lithium derivatives prepared from diethyl phenylselenomethanephosphonate with *n*-butyllithium at low temperature react with carbon tetrachloride to give the corresponding α-chlorinated phosphonate and trichloromethyllithium. The latter deprotonates the α-chlorinated phosphonate *in situ* to give a new lithio derivative which reacts with carbonyl compounds. These different steps take place in one pot and lead to chlorovinyl phenyl selenides, a novel class of selenocompounds.

In previous papers we reported the synthesis of 1,1-dichloroalkenes,[1] 1,1-dibromoalkenes,[2] 1-aryl-1-chloroalkenes[3] and aryl 1-chloro-1-alken-1-yl sulfides (chlorovinyl phenyl sulfides)[4] by an interesting one pot technique, a variation of the Horner-Emmons reaction that we named α-chlorination and carbonyl olefination. We describe here a novel application of this method to the synthesis of chlorovinyl phenyl selenides **7**.

Vinylic selenides **7** are intermediates of great synthetic potential, since they combine the ability of the double bond to form single carbon-carbon bonds with the functional transformations achieved by the well known reactions of the organoselenium compounds.[5,6] β-Chlorovinylic selenides are known,[6] but to our knowledge no preparations of compounds of type **7** have yet been described.

A suitable method for the preparation of the starting material, diethyl phenylselenomethanephosphonate **(3)**, consists in the conversion of the readily available diethyl iodomethanephosphonate **(1)**[7] into the corresponding Grignard reagent **2** using isopropylmagnesium chloride and subsequent reaction with commercial benzeneselenenyl chloride.

Compound **3**, thus obtained, was metallated with *n*-butyllithium at low temperature in tetrahydrofuran as described in reference.[8] Subsequent chlorination of the lithiated compound **4** by tetrachloromethane gave the diethyl chloro(phenylseleno) methanephosphonate **(5)** and trichloromethyllithium. The latter deprotonated **5** to give the α-chlorolithio compound **6**.

At this stage the carbanion **6** could be hydrolyzed affording the α-chlorinated product **5** (92% yield of crude product, 62% yield after distillation). The reaction of **6** with carbonyl compounds was employed for the preparation of phenyl 1-chloro-1-alken-1-yl selenides **7**. In this case the total reaction sequence **3** → **7** was achieved in one pot [in a mixture of tetrahydrofuran/hexane as solvent (Method A)], without isolation of the intermediates, in particular, without isolation of diethyl chloro(phenylseleno)-methanephosphonate **(5)**.

The lithium derivative **6** reacted with aromatic or aliphatic aldehydes as well as with ketones, like the lithium derivative of diethyl phenylthiomethanephosphonate[4] and with comparable yields. We noted that the starting product **3** completely disappeared after the introduction of tetrachloromethane and stirring for 30 min at −78 °C. Prolonged reaction times led to decomposition of **6**.

The reaction proved highly stereoselective with aromatic and aliphatic aldehydes and gives one stereoisomer only of **7**. The configuration of the phenyl 1-chloro-1-alken-1-yl selenides was not determined. With the butanone a 1:1 *E*/*Z*-mixture of the product **7h** was formed.

A second procedure (Method B) was studied to obtain the chlorovinyl phenyl selenides **7** from **3** by previously converting diethyl phenylselenomethanephosphonate **3** into **5**, following a sequence similar to that indicated above but carried out with isolated **5**. The phosphonate **5** was treated with *n*-butyllithium for 4 hours at −78 °C to give the lithium derivative **6**. Subsequent reaction of **6** with carbonyl compounds under conditions similar to those of Method A gave the chlorovinyl selenides **7**. These conditions did not increase the efficiency of the reaction: yields of vinyl selenides **7** are comparable in the two procedures A and B (Table).

The total reaction sequence **3** → **7** was also studied for one example **(7b)** under phase transfer conditions, without isolation of intermediates. The yield was however only 30%.

In summary, the above methods provide ready access to α-chlorovinyl selenides, compound of great interest as potential synthetic intermediates.

Diethyl Phenylselenomethanephosphonate (3):
A solution of Diethyl iodomethanephosphonate (**1**; 2.78 g, 10 mmol) in tetrahydrofuran (10 ml) is added dropwise at −70 °C in a nitrogen atmosphere to a 1.5 molar tetrahydrofuran solution of freshly prepared isopropylmagnesium chloride (11 mmol) in tetrahydrofuran (40 ml) and stirred for 45 min at −70 °C. Then, benzeneselenenyl chloride (1.92 g, 10 mmol) in tetrahydrofuran (10 ml) is added dropwise at −70 °C. The mixture is allowed to warm to room temperature and immediately hydrolyzed with water (40 ml). The aqueous layer is extracted with dichloromethane or chloroform (3 × 50 ml). The combined extract is dried with magnesium sulfate, and the solvent is evaporated under reduced pressure to leave the crude product **3** as an oil which is purified by distillation *in vacuo*; yield: 2.1–2.6 g (70–85%); b.p. 145 °C/0.2 torr (Lit.[8] 135 °C/0.05 torr).

^{1}H-NMR (CCl_4/TMS): δ = 1.25 (t, 6H, *J* = 6.7 Hz); 2.9 (d, 2H, *J* = 12.7 Hz); 3.7–4.4 (dq, 4H, *J* = 6.7 Hz); 7.1–7.3 (m, 3H); 7.4–7.7 ppm (m, 2H).

Phenyl 1-Chloro-1-alken-1-yl Selenides 7, Method A; General Procedure:
In an argon atmosphere a 2.6 molar solution of *n*-butyllithium in hexane (2.75 ml, 7.15 mmol) is added dropwise at −78 °C to diethyl phenylselenomethanephosphonate (2 g, 6.5 mmol) in tetrahydrofuran (20 ml). The mixture is stirred at −78 °C for 4 h, tetrachloromethane (1.1 g, 7.15 mmol) in tetrahydrofuran (10 ml) is added and stirring is continued for 30 min during which time the solution acquires a yellow

Table. Preparation of Phenyl 1-Chloro-1-alken-1-yl Selenides **7**[a]

Product No.	R^1	R^2	Method	Yield (%)	Molecular Formula[b]	^{1}H-NMR (CCl_4/TMS) δ (ppm)
7a	*p*-$CH_3C_6H_4$	H	A	58	$C_{15}H_{13}ClSe$ (307.7)	2.2 (s, 3H); 6.5–8.0 (m, 10H)
7b	*p*-$CH_3OC_6H_4$	H	A	60	$C_{15}H_{13}ClOSe$ (323.7)	3.8 (s, 3H); 6.6–7.9 (m, 10H)
			B	61		
7c		H	B	67	$C_{15}H_{11}ClO_2Se$ (337.7)	5.9 (s, 2H); 6.5–8.0 (m, 9H)
7d	*m*-ClC_6H_4	H	A	56	$C_{14}H_{10}Cl_2Se$ (328.1)	6.5–8.0 (m, 10H)
			B	53		
7e	*p*-ClC_6H_4	H	A	55	$C_{14}H_{10}Cl_2Se$ (328.1)	6.6–8.0 (m, 10H)
7f	*i*-C_3H_7	H	A	57	$C_{11}H_{13}ClSe$ (259.6)	1.0 (dd, 6H, J = 6.6 Hz); 2.6–3.3 (m, 1H); 6.18 (d, 1H, J = 9.1 Hz); 7.0–7.7 (m, 5H)
7g	*n*-C_6H_{13}	H	A	51	$C_{14}H_{19}ClSe$ (301.7)	0.6–2.0 (m, 11H); 2.0–2.6 (m, 2H); 6.3 (t, 1H, J = 6.6 Hz); 6.9–7.8 (m, 5H)
7h	C_2H_5	CH_3	A	50	$C_{11}H_{13}ClSe$ (259.6)	1.02 (t, 3H, J = 7.0 Hz); 1.07 (t, 3H, J = 7.0 Hz); 2.0 (s, 3H); 2.06 (s, 3H); 2.40 (q, 2H, J = 7.0 Hz); 2.42 (q, 2H, J = 7.0 Hz); 7.0–7.7 (m, 5H)
7i	*c*-C_6H_{11}		A	62	$C_{13}H_{15}ClSe$ (285.7)	1.6 (m, 6H); 2.55 (m, 4H); 7.0–7.7 (m, 5H)
			B	63		

[a] All compounds were obtained as oil and purified by column chromatography.

[b] Satisfactory microanalyses were obtained for **7b**, **7c**, **7h**, **7i**: C ±0.42, H ±0.20, Cl ±0.40. For **7a**, **7d**, **7e**, **7f**, **7g** satisfactory microanalyses were obtained for carbon and hydrogen atoms, C ±0.50; H ±0.30, but the analyses values are not reproductible for the same sample relative to the chlorine atom and are far outside of the normally accepted limits of precision. Apparently the chlorovinyl selenides have low stability and slowly degrade.

[c] The product **7h** is a mixture of *Z*- and *E*-stereoisomers (*Z*/*E* = 1/1).

color indicating the formation of the lithiated anion **6**. The carbonyl compound (6.5 mmol) in tetrahydrofuran (10 ml) is added, stirring is continued at −78 °C for 1 h and at room temperature for 1 h. The mixture is then hydrolyzed by addition of water (25 ml). The product is extracted with ether (3 × 30 ml), the combined organic layer is dried with magnesium sulfate, and the solvent is removed under reduced pressure. The residue is purified by column chromatography on silica gel using hexane as eluent to give the product **7** as an oil (Table).

Diethylphenylselenochloromethane Phosphonate (5):
To the yellow solution of the lithiated anion **6** prepared as described above, water (20 ml) is added. The mixture is extracted with dichloromethane (3 × 30 ml), the combined organic extract is dried with magnesium sulfate, the solvent is removed under reduced pressure, and the residue distilled *in vacuo*; yield: 3.1 g (92%; crude product); 62% after distillation; b.p. 155 °C/0.2 torr.

$C_{11}H_{16}ClO_3PSe$ (341.6) calc. C 38.65 H 4.68 Cl 10.39 P 9.08
found 38.94 4.76 10.38 9.16

^{1}H-NMR (CCl_4/TMS): δ: 1.37 (t, 6H, J = 6.7 Hz); 4.2 (dq, 4H, J = 6.7 Hz); 5.0 (d, 1H, J = 10.0); 7.1–7.5 (m, 3H); 7.5–8.0 ppm (m, 2H).

Phenyl 1-Chloro-1-alken-1-yl Selenides 7. Method B; General Procedure:
A 2.6 molar solution (2.75 ml, 7.15 mmol) of *n*-butyllithium in hexane is added dropwise at −78 °C to diethyl phenylselenochloromethanephosphonate **5** (2.2 g, 6.5 mmol), obtained as described above, in tetrahydrofuran (20 ml). The mixture is stirred at −78 °C for 4 h. Then the carbonyl compound (6.5 mmol) in tetrahydrofuran (10 ml) is added and the procedure is continued exactly as described above for Method A (Table).

Phenyl [1-Chloro-2-(*p*-methoxyphenyl)ethenyl]-1-yl Selenide (7b):
A mixture of selenophosphonate **3** (0.86 g, 2.8 mmol), *p*-methoxybenzaldehyde (0.34 g, 2.5 mmol), carbontetrachloride (5.2 ml) and benzyltriethylammonium bromide (0.11 g, 0.4 mmol) is added to a vigorously stirring 50% aqueous solution of sodium hydroxide (4 ml). The temperature of the mixture increases slightly (up to 30 °C), and the stirring is continued for 1 h. The mixture is diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined organic layer is washed with water (20 ml), dried with magnesium sulfate, and the solvent is removed under reduced pressure. The product is purified by column chromatography on silica gel using hexane as eluent.

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