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THE REACTION OF SELENOPHOSPHONATES WITH CARBONYL COMPOUNDS. VINYLIC SELENIDES

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Summary

Selenophosphonates of the general formula $(EtO)_2P(O)CHRSePh$ were prepared and their reactions with aldehydes and ketones investigated. The products formed are vinylic selenides having predominantly the *E* configuration. Hydrolytic cleavage of these products gives the corresponding ketones.

Introduction

The Horner—Wittig reaction of α-thio- [1—5], α-sulphinyl- [3,4,6], or α-sulphonyl- [3,4,7] phosphonates, as well as α-thiophosphine oxides [8] with carbonyl compounds, recently has attracted considerable attention due to the utility of the vinylic derivatives in subsequent transformations.

It is well known that vinylic sulphides are easily converted to ketones by hydrolysis [2,9]. More recently, α,β-unsaturated sulphones have been desulphurated to the corresponding olefins [10].

We previously [11—13] reported the synthesis of vinylic selenides by Wittig reactions of selenophosphoranes with aldehydes (eq. 1) as well as preliminary

$$Ph_3P{=}CRSePh + R'CHO \rightarrow R'CH{=}CRSePh + Ph_3PO \qquad (1)$$

results [12,13] regarding similar Horner—Wittig reactions. In this paper, we report a more complete investigation of this latter reaction (eq. 2).

$$(EtO)_2P(O)\bar{C}RSePh + R'R''CO \rightarrow R'R''C{=}CRSePh + (EtO)_2PO_2^- \qquad (2)$$

This method for the preparation of vinyl selenides complements the other known routes [14—18] to these important synthetic intermediates.

Results and discussion

The starting material was diethyl phenylselenomethylphosphonate (I), which was prepared from diethyl iodomethylphosphonate and PhSeNa (eq. 3).

$$(EtO)_2P(O)CH_2I + PhSeNa \rightarrow (EtO)_2P(O)CH_2SePh \qquad (3)$$

(I)

Alkylation of I was achieved in good yields by deprotonation with BuLi and subsequent reaction with the appropriate alkyl halides, promising a wide aplicability of this class of reagents (eq. 4).

$$(EtO)_2P(O)CH_2SePh \xrightarrow[(2)\ RX]{(1)\ BuLi} (EtO)_2P(O)CHRSePh \qquad (4)$$

(I) (II)

Another potential selenoolefination reagent, the phenylselenophosphine oxide III, can be prepared readily by phenylselenation of diphenylbenzylphosphine oxide (eq. 5), III being a potential reagent for the preparation of α-selenostyryl derivatives.

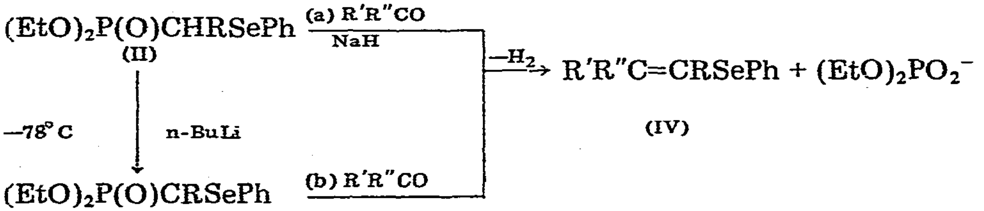
$$Ph_2P(O)CH_2Ph \xrightarrow[(2)\ PhSeBr]{(1)\ BuLi} Ph_2P(O)CH(SePh)Ph \qquad (5)$$

(III)

The olefination step can be achieved by either of two methods (eq. 6):

(a) Treatment of a mixture of the phosphonate and of the carbonyl compound with NaH in boiling THF/HMPA *. In accordance with previous reports [1,19,20], no reaction was observed when the phosphonates were heated alone with NaH.

(b) Deprotonation of the phosphonate with n-butyllithium at low temperature in THF, followed by treatment with the carbonyl compound.



$$\begin{tikzcd} \underset{(II)}{(EtO)_2P(O)CHRSePh} \arrow[d, "n\text{-BuLi}", "-78^\circ C"'] \arrow[rr, "(a)\ R'R''CO", "NaH"'] & & \underset{(IV)}{R'R''C{=}CRSePh} + (EtO)_2PO_2^- \quad (6) \\ (EtO)_2P(O)CRSePh \arrow[rru, "(b)\ R'R''CO"', "-H_2"] & & \end{tikzcd}$$

From Table 1, it can be seen that the yields of the olefination reactions are generally high in the case of aromatic aldehydes, decreasing from about 80% to about 50% with increasing length of the chain R in II. Both methods a and b can be employed.

Aliphatic aldehydes give the expected IV in acceptable yields. Not surprisingly, only method b can be employed, since prolonged heating in the presence of NaH promotes self-condensation of the aldehyde, leading to recovery of the starting selenophosphonate.

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* HMPA = hexamethylphosphinetriamide, $(Me_2N)_3PO$.

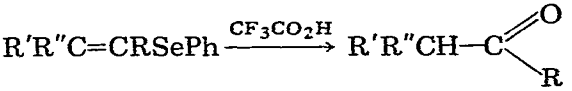
Ketones also participate in the olefination reaction; cyclohexanone, cycloheptanone and benzophenone gave 50—80% yields of IV. Even easily enolizable ketones such as 3-pentanone and acetophenone furnished the desired product IV in good yields, self condensation products not being observed.

Finally, we observed that the phosphine oxide III is unreactive under our conditions, being recovered unchanged.

In connection with the analogous reactions, mentioned above, of α-thiophosphonates with carbonyl compounds, it seems that somewhat conflicting results, which are in disagreement, at least in some degree with our findings concerning the selenium analogs, have been reported. While some authors describe reactions with aldehydes as well as ketones [1,2,5], others restrict the reactivity to only aromatic aldehydes [3,4]. With regard to the reactions of diphenylphosphinoyl derivatives, the observed inertness of our compound III, in contrast to the reactivity of α-thiophosphine oxides, $Ph_2P(O)CHRSPh$ [8], is certainly attributable to the stabilizing effect of the phenyl group of III.

A pronounced stereoselectivity for the *E* isomer was observed in the reactions of selenophosphonates with aldehydes (>90%, see Table 2), as normally expected for Horner—Wittig reactions [21]. Assignment of the *E* configuration was made on the basis of NMR spectra and GLC data (Table 2). In all the cases, the retention time of the *Z* isomer was shorter than that of the *E* isomer. The stereochemistry of the olefination reaction seems to be solvent-dependent. When performed in a 1/1 THF/HMPA mixture or in pure HMPA, the olefinic products exhibited an increased *Z/E* ratio (Table 2, entries 1, 4).

The applicability of these reactions as a route for the synthesis of ketones, through hydrolysis of the vinylic selenides IV, was examined. In addition to the $HgCl_2/CH_3CN/H_2O$ reagent, previously employed [11], we were able to achieve hydrolysis using trifluoroacetic acid. This reagent, also used for vinylic sulphides [8], appears to be more practical, since shorter reaction times at room temperature are sufficient * (eq. 7).



$$\underset{\text{(IV)}}{R'R''C{=}CRSePh} \xrightarrow{CF_3CO_2H} R'R''CH{-}C\overset{\displaystyle O}{\underset{\displaystyle R}{\lessgtr}} \qquad (7)$$

As previously described for the analogous thio derivatives [2,9], aldehydes cannot be obtained by this method since the corresponding α-unsubstituted compounds (IV, R = H) are stable toward hydrolysis.

An interesting extension of this work is the preparation of the divinylic selenide VI by reaction of the bis-phosphonate V, prepared from sodium selenide and diethyl iodomethylphosphonate, with benzaldehyde ** (eq. 8).

$$2\,(EtO)_2P(O)CH_2I + Na_2Se \rightarrow \underset{\text{(V)}}{(EtO)_2P(O)CH_2SeCH_2P(O)(OEt)_2}$$

$$V \xrightarrow[2\,PhCHO]{NaH} \underset{\text{(VI)}}{PhCH{=}CH{-}Se{-}CH{=}CHPh} \qquad (8)$$

(continued on p. 302)

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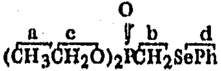
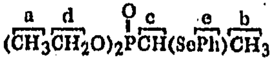
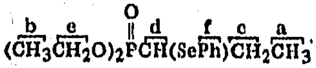
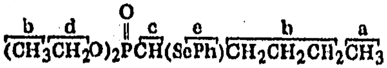
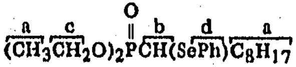
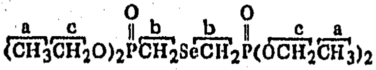
* A systematic study of the hydrolysis of vinylic selenides is in progress.

** The use of the bis-phosphonate V for the preparation of cyclic compounds is under investigation.

TABLE 1

PREPARATION OF SELENOBENZYLPHOSPHINE OXIDES

	Yield (%)	B.p. (°C/mmHg)	Analysis Found (calcd.) (%)		^{1}H NMR (δ (ppm), J (Hz), TMS internal reference)
			C	H	
1.  $(\overbrace{CH_3}^{a}\overbrace{CH_2O}^{c})_2\overset{\overset{O}{\|}}{P}\overbrace{CH_2}^{b}Se\overbrace{Ph}^{d}$	79 89 ^{a}	135/5 X 10^{-2}	42.59 (43.03)	5.57 (5.54)	a 1.26 (6H, t, J_{ac} 7) b 2.90 (2H, d, J(PH) 13) c 4.03 (4H, dq, J(PH) 8, J_{ca} 7) d 7.1—7.3 (3H, m) 7.4—7.7 (2H, m)
2.  $(\overbrace{CH_3}^{a}\overbrace{CH_2}^{d}O)_2\overset{\overset{O}{\|}}{P}\overbrace{CH}^{c}(Se\overbrace{Ph}^{e})\overbrace{CH_3}^{b}$	94 ^{b}	120/10^{-2}	44.62 (44.90)	6.10 (5.92)	a 1.30 (6H, t, J_{ad} 7) b 1.60 (3H, dd, J(PH) 16 J_{bc} ~8) c 3.22 (1H, sex., J(PH) 16 J_{cb} ~8) d 3.9—4.3 (4H, m) e 7.1—7.3 (3H, m) 7.4—7.7 (2H, m)
3.  $(\overbrace{CH_3}^{b}\overbrace{CH_2}^{e}O)_2\overset{\overset{O}{\|}}{P}\overbrace{CH}^{d}(Se\overbrace{Ph}^{f})\overbrace{CH_2}^{c}\overbrace{CH_3}^{a}$	74	125/2 X 10^{-2}	47.00 (46.60)	6.56 (6.26)	a 1.13 (3H, t, J_{ac} 7) b 1.33 (6H, t, J_{be} 7) c 1.6—2.3 (2H, m) d 2.6—3.1 (1H, m) e 3.8—4.4 (4H, m) f 7.1—7.3 (3H, m) 7.4—7.7 (2H, m)
4.  $(\overbrace{CH_3}^{b}\overbrace{CH_2}^{d}O)_2\overset{\overset{O}{\|}}{P}\overbrace{CH}^{c}(Se\overbrace{Ph}^{e})\overbrace{CH_2CH_2CH_2}^{b}\overbrace{CH_3}^{a}$	71	133/3 X 10^{-2}	50.00 (49.62)	7.35 (6.88)	a 0.88 (3H, t, J 7) b 1.1—2.2 (12H, m) c 2.8—3.2 (1H, m) d 3.9—4.4 (4H, m) e 7.1—7.3 (3H, m) 7.4—7.7 (2H, m)
5.  $(\overbrace{CH_3}^{a}\overbrace{CH_2}^{c}O)_2\overset{\overset{O}{\|}}{P}\overbrace{CH}^{b}(Se\overbrace{Ph}^{d})\overbrace{C_8H_{17}}^{a}$	74 ^{b}	150/10^{-2}	54.00 (54.44)	7.89 (7.87)	a 0.7—2.1 (23H, m) b 2.6—3.1 (1H, m) c 3.8—4.4 (4H, m) d 7.1—7.3 (3H, m) 7.4—7.7 (2H, m)
6.  $(\overbrace{CH_3}^{a}\overbrace{CH_2}^{c}O)_2\overset{\overset{O}{\|}}{P}\overbrace{CH_2}^{b}Se\overbrace{CH_2}^{b}\overset{\overset{O}{\|}}{P}(\overbrace{OCH_2}^{c}\overbrace{CH_3}^{a})_2$	70 ^{b}	145/5 X 10^{-3}	31.20 (31.52)	6.13 (6.30)	a 1.33 (12H, t, J_{ac} 7) b 2.91 (4H, d, J(PH) 11) c 4.10 (8H, dq, J(PH) ~8, J_{ca} 7)

$7.\ \overset{b}{\overline{Ph_2}}\overset{O}{\overset{\|}{P}}\overset{a}{\overline{CH}}(Se\overset{b}{\overline{Ph}})\overset{b}{\overline{Ph}}$	70	197–199 [d]	67.41 (67.14)	4.70 (4.70)	a 3.62 (1H, d, J(PH) 14) [c] b 7.0–7.8 (20H, m)

[a] Prepared by method b. Yield after purification by Column Chromatography. [b] Distilled in "Kugelrohr". [c] Spectra registered in $CDCl_3$ on a XL 100 spectrometer. [d] Recrystallized from ethanol.

TABLE 2

PREPARATION OF VINYLIC SELENIDES

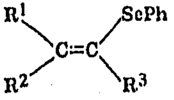
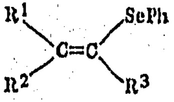
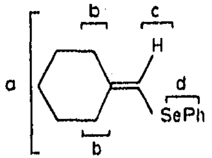
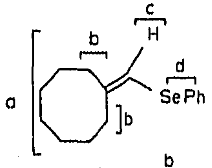
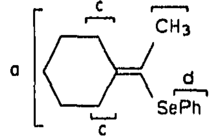
	Yield (%)	B.p. (°C/mmHg) [c] or m.p. (°C)	Analyses found (calcd.) (%)		Reaction time (h)	Z/E ratio	^1H NMR data (for main isomer E) (δ (ppm), J (Hz), TMS internal reference)
			C	H			
$1.\ \overset{d}{\overline{Ph}}\overset{a}{\overline{CH}}=\overset{b}{\overline{CH}}Se\overset{c}{\overline{Ph}}$	80 [a] 70 [b]	100–105/ 5×10^{-2}	[11]		1.5 16	6/94 16/84 [e]	a 6.70 (1H, d, J_{ab} 15) b 7.12 (1H, d, J_{ba} 15) c 7.0–7.6 (10H, m)
$2.\ p\text{-}\overset{a}{\overline{CH_3}}\overset{d}{\overline{Ph}}\overset{b}{\overline{CH}}=\overset{c}{\overline{CH}}Se\overset{d}{\overline{Ph}}$	72 [a]	$122/10^{-2}$	[11]		1.5	8/92	a 2.30 (3H, s) b 6.73 (1H, d, J 16) c 7.06 (1H, d, J 16) d 7.1–7.6 (10H, m)
$3.\ p\text{-}NO_2PhCH{=}CHSePh$	74 [b]	67–76 [f]	[11]		17 r.t.	4/96	a 6.60 (1H, d, J 16) b 7.0–8.3 (14H, m) [h]
$4.\ \overset{c}{\overline{Ph}}\overset{b}{\overline{CH}}=C(Se\overset{c}{\overline{Ph}})\overset{a}{\overline{CH_3}}$	86 [a]	$110/5 \times 10^{-3}$	[11]		6	13/87 47/53 [e]	a 2.20 (3H(d, J_{ab} 1.5) b 6.76 (1H, q, J_{ba} 1.5) c 7.1–7.6 (10H, m)
$5.\ p\text{-}\overset{b}{\overline{CH_3}}\overset{d}{\overline{Ph}}\overset{c}{\overline{CH}}=C(Se\overset{d}{\overline{Ph}})\overset{a}{\overline{CH_3}}$	70 [a]	$127/5 \times 10^{-2}$	[11]		6	8/92	a 2.18 (3H, d, $J \sim 1.5$) b 2.30 (3H, s) c 6.80 (1H, s, br) d 7.0–7.7 (9H, m)
$6.\ \overset{d}{\overline{Ph}}\overset{c}{\overline{CH}}=C(Se\overset{d}{\overline{Ph}})\overset{b}{\overline{CH_2}}\overset{a}{\overline{CH_3}}$	70 [a]	$120/10^{-2}$	[11]		6	8/92	a 1.20 (3H, t, J_{ab} 7) b 2.50 (2H, q, J_{ba} 7) c 6.76 (1H, s) d 7.0–7.6 (10H, m)
$7.\ p\text{-}\overset{b}{\overline{CH_3}}\overset{e}{\overline{Ph}}\overset{d}{\overline{CH}}=C(Se\overset{e}{\overline{Ph}})\overset{c}{\overline{CH_2}}\overset{a}{\overline{CH_3}}$	51 [a]	$140/10^{-2}$	67.50 (67.80)	5.71 (5.97)	6	18/82	a 1.16 (3H, t, J 7) b 2.30 (3H, s) c 2.46 (2H, q, J 7) d 6.73 (1H, s, br) e 7.0–7.6 (9H, m)

TABLE 2 (continued)

	Yield (%)	B.p. (°C/mmHg) ^{c} or m.p. (°C)	Analyses found (calcd.) (%)		Reaction time (h)	Z/E ratio	^{1}H NMR data (for main isomer E) (δ (ppm), J (Hz), TMS internal reference)
			C	H			
8. $\overset{d}{\overline{Ph}}\overset{c}{\overline{CH}}=C(\overset{d}{\overline{SePh}})\overset{b}{\overline{CH_2}}\overset{a}{\overline{CH_2CH_2CH_3}}$	66 ^{a}	135/2 × 10^{-2}	68.26 (68.59)	5.88 (6.34)	1.5	25/75	a 0.6–1.8 (7H, m) b 2.45 (2H, t, J_{bc} ~7) c 6.78 (1H, s) d 7.0–7.7 (10H, m)
9. p-$\overset{c}{\overline{CH_3}}\overset{e}{\overline{Ph}}\overset{d}{\overline{CH}}=C(\overset{e}{\overline{SePh}})\overset{b}{\overline{CH_2}}\overset{a}{\overline{CH_2CH_2CH_3}}$	55 ^{a}	118/4 × 10^{-3}	68.90 (69.32)	6.84 (6.68)	6	25/75	a 0.6–1.9 (7H, m) b 2.1–2.7 (2H, m) c 2.30 (2H, s, br) d 6.73 (1H, s, br) e 6.9–7.7 (9H, m)
10. p-$\overset{c}{\overline{CH_3}}\overset{e}{\overline{Ph}}\overset{d}{\overline{CH}}=C(\overset{e}{\overline{SePh}})\overset{b}{\overline{CH_2}}\overset{a}{\overline{C_7H_{15}}}$	52 ^{a}	145/4 × 10^{-3}	71.52 (71.71)	7.37 (7.78)	6	23/77	a 0.7–1.8 (15H, m) b 2.1–2.6 (2H, m) c 2.30 (3H, s) d 6.76 (1H, s, br) e 6.9–7.7 (9H, m)
11. $\overset{a}{\overline{CH_3}}\overset{b}{\overline{CH_2}}\overset{c}{\overline{CH_2}}\overset{d}{\overline{CH}}=\overset{e}{\overline{CH}}\overset{f}{\overline{SePh}}$	57 ^{b}	90/6 × 10^{-2}	58.84 (58.70)	6.84 (6.22)	15	5/95	a 0.88 (3H, t, J_{ab} ~7) b 1.1–1.7 (2H, m) c 2.10 (2H, q, J_{cb} = J_{cd} ~7) d 5.91 (1H, dt, J_{de} 14, J_{dc} ~7) e 6.41 (1H, d, J_{ed} 14) f 7.0–7.5 (5H, m)
12. $\overset{c}{\overline{Ph}}\overset{a}{\overline{CH}}=\overset{b}{\overline{CH}}Se\overset{b}{\overline{CH}}=\overset{a}{\overline{CH}}\overset{c}{\overline{Ph}}$ ^{f}	77 ^{a}	43–45	67.00 (67.39)	4.76 (4.91)	2	^{i}	a 6.78 (2H, d, J 16) b 7.13 (2H, d, J 16) c 7.2–7.4 (10H, m) ^{g}
13. $\overset{a}{\overline{CH_3(CH_2)_4}}\overset{b}{\overline{CH_2}}\overset{c}{\overline{CH}}=\overset{d}{\overline{CH}}\overset{e}{\overline{SePh}}$	45 ^{a}	95/5 × 10^{-3}	[11]		15	5/95	a 0.4–1.7 (11H, m) b 1.9–2.4 (2H, m) c 6.00 (1H, dt, J_{cd} 15, J_{cb} ~7) d 6.38 (1H, d, J_{dc} 15) e 7.0–7.6 (5H, m)

14. $\overset{c}{\overline{Ph}}C(\overset{a}{\overline{CH_3}})=\overset{b}{\overline{CH}}Se\overset{c}{\overline{Ph}}$	$<10^{a}$ 50^{b}	$115/5 \times 10^{-3}$	65.45 (65.96)	5.26 (5.12)	20 15	^{j}	a 2.20 (3H, s, br) b 6.73 (1H, s, br) c 7.0–7.5 (10H, m)
15. $(\overset{a}{\overline{CH_3}}\overset{b}{\overline{CH_2}})_2C=\overset{c}{\overline{CH}}Se\overset{d}{\overline{Ph}}$	$<10^{a}$ 70^{b}	$90/2 \times 10^{-2}$	59.86 (60.28)	6.59 (6.69)	20 15		a 0.9–1.3 (6H, m) b 1.9–2.5 (4H, m) c 6.08 (1H, t, J_{cb} ~1) d 7.0–7.5 (5H, m)
16. 	52^{a} 78^{b}	$112/10^{-2}$	62.42 (62.19)	6.58 (6.37)	4 15		a 1.3–1.8 (6H, m) b 2.0–2.5 (4H, m) c 6.06 (1H, s, br) d 7.0–7.5 (5H, m)
17. 	50^{a}	$120/10^{-2}$	64.10 (64.56)	7.57 (7.16)	4		a 1.3–2.0 (10H, m) b 2.1–2.5 (4H, m) c 6.16 (1H, s, br) d 7.0–7.5 (5H, m)
18. 	60^{a}	$125/2 \times 10^{-2}$	63.00 (63.42)	7.12 (6.78)	4		a 1.4–1.8 (6H, m) b 2.10 (3H, s, br) c 2.2–2.8 (4H, m) d 7.0–7.6 (5H, m)
19. $\overset{b}{\overline{Ph_2}}C=\overset{a}{\overline{CH}}Se\overset{b}{\overline{Ph}}$ ^{f}	52^{a}	81.5–82	71.70 (71.66)	4.87 (4.77)	4		a 7.03 (1H, s) b 7.1–7.7 (15H, m)

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[a] THF/HMPA$_6$ method a. [b] THF, –78°, method b. [c] Distilled in "Kugelrohr". [d] ^{1}H NMR spectra registered on a XL100 spectrometer. [e] Reaction performed in pure HMPA. [f] Recrystallized from ethanol. [g] Two peaks of low intensities appear respectively at δ 6.75 and 7.10. [h] ^{1}H NMR spectra registered in CDCl$_3$. [i] Two peaks with 71 : 29 ratio observed in GLC. [j] A single peak in the GLC.

The conversion $(EtO)_2P(O)CH_2SePh \rightarrow \rightarrow \rightarrow H-\overset{\diagdown\diagup}{C}-C(O)R$ described here, constitutes a valuable contribution to the methodology of ketone synthesis. In relation to our previous studies of the selenophosphorane route to vinylic selenides [11], the present route offers the advantage of wider applicability due to the simple and general alkylation of the selenophosphonates (I → II) and the reactivity of the latter with ketones.

Experimental

Gas liquid chromatographic (GLC) analyses were performed on a Varian 2800 instrument equipped with flame ionization detector and 5′ × 1/8″ column (of 3% SE 30 or 10% FFAP) on 60/80 Chromosorb W. ^1H NMR spectra were recorded on Varian T60 and XL 100 spectrometers, using tetramethylsilane as internal standard. Unless specified otherwise, the spectra were measured in CCl_4 solution. Melting points were determined on a Kofler hot plate apparatus and are uncorrected.

Selenophenol [22], diphenyl diselenide [23], phenylselenenyl bromide [11] and diethyl iodomethylphosphonate [24] were prepared by literature procedures.

Diethylphenylselenomethylphosphonate (I)

(a) To a suspension of NaH (2.10 g, 50 mmol, of a 57% suspension in oil, washed with hexane) in 20 ml of THF, under a nitrogen atmosphere, was added dropwise, with magnetic stirring at room temperature, selenophenol (7.5 g, 50 mmol) in 20 ml of THF. After 15 min, the resulting suspension was added dropwise at room temperature to a solution of diethyl iodomethylphosphonate (13.2 g, 47 mmol) in 20 ml of THF. After it had been stirred for 1 h, the resulting solution was washed in turn with saturated aqueous NH_4Cl and NaCl, dried over Na_2SO_4 and evaporated. The residue was distilled in vacuo.

(b) To a solution of diphenyl diselenide (1.60 g, 5.1 mmol) in 10 ml of THF was added hypophosphorous acid (H_3PO_2, 4.2 ml) [25]. The mixture was heated at reflux for 20 min and, after cooling, extracted with benzene (25 ml). The benzene solution was treated with 50% aqueous NaOH (0.7 ml) and diethyl iodomethylphosphonate (2.78 g, 10 mmol) added to the resulting suspension. The mixture was stirred at room temperature for 3 h, washed in turn with aqueous saturated NH_4Cl and NaCl, dried over Na_2SO_4 and evaporated. The crude product was purified by filtration through a column (Silica gel 60-Merck, 25 g). The excess of diphenyl diselenide was eluted with petr. ether 30—50°, and the phosphonate I with ether. The latter was identical, by NMR spectra, with the product obtained by method a.

Alkylation of I

To compound I (4.63 g, 15 mmol) in 50 ml of THF, cooled to —78°C, was added dropwise n-BuLi (in hexane, 17 mmol) under nitrogen atmosphere. After stirring for 4 h at —78°C, a solution of the alkyl halide (20 mmol) in 20 ml of THF was added. The solution was stirred for 1 h at —78°C followed by 5 h at room temperature. The solvent was evaporated under reduced pressure and the residue diluted with ether and washed successively with saturated aqueous NH_4Cl and NaCl. After evaporation of the solvent, the crude products II were distilled in vacuo.

Diphenylphenylselenobenzylphosphine oxide (III)

Diphenylbenzylphosphine oxide (2.92 g, 10 mmol) in 40 ml of ether was treated with n-BuLi (in hexane 10 mmol) at room temperature, under nitrogen atmosphere and with magnetic stirring. After 20 min, the solution was cooled to —78°C and a solution of phenylselenenyl bromide (2.12 g, 9 mmol) in 20 ml of THF added dropwise. A colorless precipitate formed immediately. After 2 h at —78°C, the mixture was allowed to reach room temperature and the solid product removed by filtration.

Reaction of I (or II) with carbonyl compounds; preparation of vinylic selenides (IV)

(a) To a mixture of NaH (0.1 g, 2.4 mmol) of a 57% suspension in oil, washed with hexane) and phenylselenophosphonate (I or II, 2 mmol) in 10 ml of THF/HMPA (10/1), at 80°C (bath temperature) under nitrogen atmosphere, was added dropwise the carbonyl compound (2.2 mmol, pure when liquid, or dissolved in 3 ml of THF when solid). Hydrogen evolution was observed. Following reflux (times, see Table 2), the solution was cooled to room temperature, diluted with 30 ml of petr. ether 30—50°, washed in turn with saturated aqueous NH_4Cl, dried with Na_2SO_4 and evaporated. The residue was filtered through a column (Silica-gel 60-Merck, 7 g). By evaporation of the solvent, pure compounds IV were obtained. Some runs were performed employing 1/1 THF/HMPA or pure HMPA as solvents (see Table 2).

(b) A solution of the phenylselenophosphonate (I or II, 2.4 mmol) in 10 ml of THF, under nitrogen atmosphere, was treated dropwise, with magnetic stirring, at —78°C, with n-BuLi (in hexane, 2 mmol). After stirring for 4 h at —78°C, the carbonyl compound (2 mmol) was added dropwise (pure when liquid, dissolved in 3 ml of THF when solid). After 1 h at —78°C the solution was refluxed (times, see Table 2). Subsequent work-up was identical to that utilized in a. A run in which compound III was treated with benzaldehyde (following procedure a) gave only the starting III.

Bis(diethylphosphomethyl) selenide (V)

Diethyliodomethylphosphonate (13.90 g, 50 mmol) in 20 ml of THF was added to a suspension of Na_2Se (Alpha—Ventron, 3.70 g, 30 mmol) in 30 ml of THF. The resulting solution was stirred at room temperature for 2 h. Normal work-up yielded pure V.

Bis(β-styryl)selenide (VI)

A mixture of compound V (0.77 g, 2 mmol), NaH (0.2 g, 4.8 mmol of a 57% suspension in oil, washed with hexane) and benzaldehyde (0.42 g, 4 mmol) in 10 ml THF/HMPA (10/1) was heated at reflux for 2 h under nitrogen atmosphere. The mixture was worked up as described under procedure 4a giving an oil which crystallized upon addition of ethanol.

Hydrolysis of vinylic selenides (preparation of benzyl ethyl ketone)

(a) The vinylic selenide (IV, $R = C_2H_5$, $R' = C_6H_5$, $R'' = H$; 0.29 g, 1 mmol) was dissolved in CF_3CO_2H (1 ml) at room temperature. Diphenyl diselenide formed at once. After 2 h of stirring, the mixture was diluted with water, extracted with ether, and the organic layer washed several times with water, dried with Na_2SO_4 and evaporated. The residue was passed through a column (Silica gel 60-Merck, 7 g). The diphenyl diselenide was eluted with petr. ether 30—50° and the ketone with ether. Yield, 0.12 g (80%). The product was identical, by NMR spectra, with an authentic sample.

(b) The same vinylic selenide was hydrolyzed with $HgCl_2/CH_3CN/H_2O$ [2]. After 70 h heating at 80°C (bath temperature), a 95% yield of the distilled ketone was obtained.

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