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THE REACTION OF SELENENYL HALIDES WITH WITTIG REAGENTS

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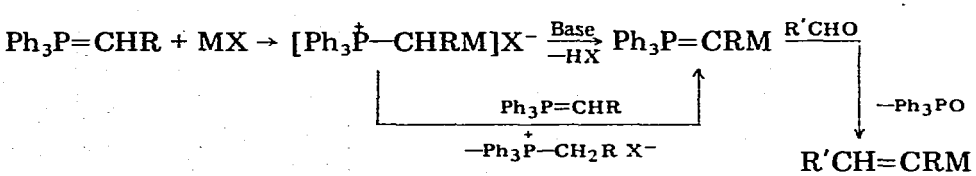
Summary

The transylidation reactions of PhSeBr with two equivalents of an alkylidenetriphenylphosphorane give selenophosphoranes, $Ph_3P{=}CRSePh$. These also can be obtained by treating the corresponding selenophosphonium salts, prepared by quaternization of triphenylphosphine with PhSeCHRBr, with n-BuLi. The selenophosphoranes react with aldehydes in situ (Wittig reaction) to give the expected vinylic selenides in good yields. The stereochemistry of the reactions is discussed.

Introduction

Since the Wittig reaction has attained great importance as an olefination method, a large number of related investigations have developed. Several of these have dealt with the reactions of alkylidenephosphoranes with metal and non-metal halides, e.g. α-substituted phosphonium salts, their conversion to the corresponding phosphoranes by treatment with suitable bases or via transylidation reactions. Several examples of Wittig reactions of such reagents with carbonyl compounds have been reported.



M = Si [1—5]; P [2,6—10]; Ge [3]; Sn [2,3,11]; Sb [4,8]; As [4,8]; Hg [1,2,12]; B [2,13]; S [14,15]

Along this line of investigation, were reported a few years ago [16] that stable arylselenophosphoranes can be prepared by a transylidation reaction between

α-carbethoxyphosphoranes and arylselenenyl bromides:

$$2\,Ph_3P{=}CHCO_2Et + ArSeBr \rightarrow Ph_3P{=}C(CO_2Et)SeAr + [Ph_3\overset{+}{P}{-}CH_2CO_2Et]Br^-$$

Ar = Ph, 2,4-$(NO_2)_2C_6H_3$

These selenophosphoranes are stabilized due to carbonyl conjugation and orbital overlap with selenium and are consequently unreactive towards aldehydes.

We have reported recently preliminary results involving similar reactions of non-stabilized phosphoranes [17]. In this paper we wish to describe a more complete study of this area.

Results and discussion

Phenylselenoalkylidenetriphenylphosphoranes

Methylene- and ethylidene-triphenylphosphorane (II), both non-stabilized phosphoranes, react with phenylselenenyl bromide in THF (step 2a) giving the selenophosphonium salt III. This then reacts with excess II in the transylidation step 2b giving the selenophosphorane IV.

$$\underset{(I)}{[Ph_3\overset{+}{P}{-}CH_2R]X^-} \xrightarrow{n\text{-BuLi}} \underset{(II)}{Ph_3P{=}CHR} \qquad (1)$$

$$Ph_3P{=}CHR + PhSeBr \rightarrow \underset{(III)}{[Ph_3\overset{+}{P}CHRSePh]Br^-} \qquad (2a)$$

$$[Ph_3\overset{+}{P}CHRSePh]Br^- + Ph_3P{=}CHR \rightarrow Ph_3P{=}\underset{(IV)}{CRSePh} + I \qquad (2b)$$

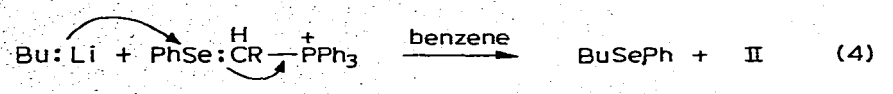
Steps 2a and 2b are very rapid, as indicated by immediate reaction of PhSeBr with phosphoranes II and the consumption of the selenophosphonium salt III as soon as it is formed. The selenophosphorane IV is soluble in the reaction medium, while the phosphonium salt I precipitates as a crystalline solid. The driving force for the transylidation step can be attributed mainly to the increased stability of the selenophosphorane IV due to the delocalization of the negative charge into the orbitals of the Se atom. This effect, well known for the 3*d* sulfur orbitals, can also be assumed for the more diffuse 4*d* orbitals of the selenium atom [18].

The quaternization of triphenylphosphine with phenyl(bromoalkyl)selenides (V) to give III [19], followed by treatment with an organolithium reagent is another way to obtain IV.

$$Ph_3P + \underset{(V)}{PhSeCHRBr} \rightarrow \underset{(III)}{[Ph_3\overset{+}{P}{-}CHRSePh]Br^-} \qquad (3a)$$

$$III \xrightarrow{n\text{-BuLi}} IV\ (R = H, CH_3) \qquad (3b)$$

Reaction 3b results in complete conversion to IV if it is performed in THF (general procedure). In some runs, however, in which benzene was employed as solvent, we observed that phenylbutylselenide was formed as a by-product (30%).



$$Bu{:}Li + PhSe{:}\overset{H}{C}R\text{—}\overset{+}{P}Ph_3 \xrightarrow{\text{benzene}} BuSePh + II \qquad (4)$$

The indiscriminate attack of BuLi on the H and on the bulkier Se atom suggests that the reagent is more reactive in benzene (although hydrocarbon solvents facilitate association) than in THF where it is more solvated. The phosphorane II, which is formed together with the selenide through the proposed mechanism, must produce in the following Wittig step a selenium-free olefin. No effort was made to isolate this more volatile by-product.

For the preparation of the phenyl(bromoalkyl)selenides (V) we tried the reaction of PhSeNa with an excess of 1,1-dihaloalkanes. Dibromomethane yielded a mixture of monosubstited Va (50%) and disubstituted VIa (45%) derivatives:

$$PhSeNa \xrightarrow[excess]{\text{(a) } Br_2CHR} PhSeCHRBr \xrightarrow{\text{(b) PhSeNa}} PhSeCHRSePh \qquad (5)$$

(Va) R = H (VIa) R = H
(Vb) R = CH_3 (VIb) R = CH_3

1,1-Dibromoethane gave only the disubstituted derivative 1,1-diselenophenylethane (VIb). The increased reactivity of a secondary selenoalkyl bromide compared with that of a primary may imply that the second step is S_N1 in character.

As an alternate approach we attempted to prepare V through the reaction of PhSeBr with the appropriate diazoalkane. High yields of the expected products were obtained (eq. 6).

$$PhSeBr + RCHN_2 \rightarrow PhSeCHRBr + N_2 \qquad (6)$$

R = H, CH_3

Methylenation of the Se—halogen bond with diazomethane has not previously been described, although similar reactions with other metal— and metalloid—halogen bonds have been extensively investigated [20]. The reaction with diazoethane was performed at 0° C, whereas diazomethane requires a lower temperature (—78° C). If the last reaction is performed at higher temperatures it led to the diseleno derivative VI as a by-product. These results are more consistent with a nucleophilic than with a carbene mechanism [20]. At low temperatures (eq. 7a—7c) the diazomethane preferentially attacks the Se atom, Br^- being the leaving group (a). At higher temperature it attacks less selectively and both Br and Se are substituted. In the latter reaction (eq. 8a—8d) a diselenide is formed as the intermediate, followed by a known methylene insertion in the Se—Se bond [21].

$$N_2^+\text{—}CH_2^-\text{:} + PhSeBr \xrightarrow[\text{low temperature}]{\text{(a)}} N_2^+\text{—}CH_2SePh + Br^- \xrightarrow{\text{(b)}}$$

$$\xrightarrow{\text{(c)}} BrCH_2SePh + N_2 \qquad (7)$$

$$N_2^+\text{—}CH_2^- + BrSePh \xrightarrow{\text{(a)}} N_2^+\text{—}CH_2Br + PhSe^-$$

$$PhSe^- + PhSeBr \xrightarrow{\text{(b)}} PhSeSePh + Br^- \xrightarrow{\text{(c)}} Br_2CH_2 + N_2$$

$$PhSeSePh + CH_2N_2 \xrightarrow{\text{(d)}} PhSeCH_2SePh + N_2 \qquad (8)$$

The Wittig reaction

The selenophosphoranes IV obtained by these two methods were not isolated but were treated in situ with aldehydes to form vinylic selenides (VII) via the Wittig reaction.

$$Ph_3P{=}CRSePh + R'CHO \rightarrow R'CH{=}CRSePh + Ph_3PO \quad (9)$$

(VII)

In the first procedure in which the Wittig reagent was prepared by transylidation, the reaction mixture normally was not filtered to remove the insoluble phosphonium salt I before the Wittig step. This did not affect the final yields. As can be observed in Table 1, the yields are very high for aromatic aldehydes, with no significant difference due to the *para* substituent, and are in the 65% range for aliphatic aldehydes. These lower yields in Wittig reactions with aliphatic aldehydes have previously been attributed to the tendency of these carbonyl compounds to undergo aldol condensation with basic reagents [22].

As normally expected for Wittig reactions, a mixture of isomers was obtained in all reactions. Table 2 summarizes the isomeric ratio for all the runs performed by the normal procedure in THF (and in the presence of Li salts). The *cis/trans* ratio of product VIIa was established by comparative gas—liquid chromatography (GLC) with authentic samples of the *cis* and *trans* isomers. These were prepared

TABLE 1

PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS VII OBTAINED BY VARIOUS METHODS

$Ph_3P{=}CRSePh + R'CHO \rightarrow R'CH{=}CRSePh + Ph_3PO$

(IV) (VII)

R	R′	Product	Method [a]	Yield (%)	B.p. (°C) or m.p. (°C/mmHg)	Analyses: found (Calcd.) (%)	
						C	H
H	Ph	VIIa	a	98	100—105/0.05	64.93	4.78
			b	99		(64.87)	(4.67)
H	*p*-CH_3Ph	VIIb	a	95	122/0.01 [b]	65.69	5.08
						(65.94)	(5.16)
H	*p*-NO_2Ph	VIIc	a	87	70—100	55.34	3.55
			b	90		(55.28)	(3.64)
H	CH_3CH_2	VIId	a	66	60—65/1	56.89	6.12
						(56.88)	(5.73)
H	$CH_3(CH_2)_5$	VIIe	a	65	81—85/0.01 [b]	62.52	7.61
						(62.91)	(7.54)
CH_3	Ph	VIIf	a	99	110—115/0.005	65.68	5.27
						(65.97)	(5.61)
CH_3	*p*-CH_3Ph	VIIg	a	95	127/0.05 [b]	66.68	5.64
						(66.90)	(5.61)
CH_3	*p*-NO_2Ph	VIIh	a	91	54—84	56.24	3.99
			b	90		(56.61)	(4.12)
CH_3	CH_3CH_2	VIIi	a	65	75—80/5	58.47	6.12
						(58.67)	(6.27)
CH_3	$CH_3(CH_2)_5$	VIIj	a	63	65—70/0.25	63.95	7.58
						(64.05)	(7.88)

[a] a, transylidation; b, Se phosphonium salts + BuLi. [b] Distilled in "short path".

by addition of PhSeH to phenylacetylene (eq. 10) [23,24] and by stereospecific $LiAlH_4$ reduction of the phenyl(phenylseleno)acetylene (VIII) (eq. 11) [25,26], respectively.

$$PhC{\equiv}CH + PhSeH \rightarrow \underset{\text{(VIIa)}}{PhCH{=}CHSePh\ (cis)} \qquad (10)$$

$$PhC{\equiv}CH \xrightarrow[(2)\ PhSeBr]{(1)\ n\text{-}BuLi} \underset{\text{(VIII)}}{PhC{\equiv}CSePh} \xrightarrow{LiAlH_4} \underset{\text{(VIIa)}}{PhCH{=}CHSePh\ (trans)} \qquad (11)$$

The isomer mixtures for compounds VIIb and VIIc exhibited a strong IR band at 945 cm^{-1}. A smaller band at 944 cm^{-1} has been shown to be characteristic for the *trans* isomer of VIIa and completely absent in *cis*-VIIa [23]. These data suggested that the major peak in GLC for (VIIb) and (VIIc) compounds corresponded to the *trans* isomer. Confirmatory evidence was obtained by GLC comparison with pure samples of the *trans* isomer prepared by the Horner—Wadsworth and Emmons phosphonate method *. The isomeric ratio for compounds (VIIf—VIIh) could not be established from spectroscopic data due to the lack of related information **. The preparation of authentic *trans* isomers by Horner—Wadsworth and Emmons reaction (as was done for (VIIb, c)) would confirm this.

From the data summarized in Table 2 it can be seen that selenophosphoranes are devoid of marked stereoselectivity with aromatic aldehydes (although the *trans* isomer is the major product) and are non-stereoselective with aliphatic aldehydes.

Compounds (VIIa, VIId and VIIe) also were prepared in salt-free benzene medium (performing the reactions in benzene and filtering before the addition of the aldehyde) and the isomeric data were established by comparative GLC. For this purpose the pure *trans*- VIId and *trans*- VIIe compounds were prepared by the mentioned phosphonate method. The results are summarized in Table 2. It can be seen that under salt-free conditions, benzaldehyde gives more *cis* isomer, whereas aliphatic aldehydes give more *trans* isomer.

Competitive reactions performed under salt-free conditions between IV (R = H) and a 1 : 1 mixture of benzaldehyde and propionaldehyde showed that the former reacts faster than the latter.

These preliminary data seem to support the idea that selenophosphoranes are on the borderline between stable and reactive ylides. The increased reactivity with aromatic vs. aliphatic aldehydes agrees with a reactive ylid character involving the classical two steps, attack of the phosphorane on the aldehydes, giving a betaine, and decomposition of the betaine to the olefin and Ph_3PO. Both steps are irreversible and the decomposition of the intermediate betaine to

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* We also prepared compounds (VIIb—VIIe) by the Horner—Wadsworth—Emmons reaction between $(EtO)_2P(O)CH_2SePh$ and the appropriate aldehydes. Isomerically pure compounds were obtained and were assumed to be the *trans* isomer as is normally observed for Horner—Wadsworth—Emmons reactions [27].

** Since the tables of Pascual, Meier and Simon [28] lack data-correlating chemical shifts of olefinic protons with SeR substituents, we were unable to employ NMR spectral informations to elucidate this question.

the products is favored by conjugation in the final olefin *. Furthermore the *cis* isomer is a major kinetically-controlled product in a salt-free reaction with benzaldehyde. The presence of Li salts allows some equilibration between the *erythro*- and *threo*-betaine, and a thermodynamical controlled process produces more *trans* olefin [31—33].

On the other hand, the reversibility factor should increase in the slower reactions with aliphatic aldehydes and more of the kinetically favored *erythro*-betaine should be converted into the *threo* isomer, giving the *trans* olefin as the main product. The presence of Li salts hinders the conversion of the *erythro*- to the *threo*-betaine, giving increased (but not predominant) formation of the *cis* isomer (as occurs for stable ylides). The result of this delicate balance is a lack of stereoselectivity. Investigations are in progress, which will provide a more thorough understanding of the problem.

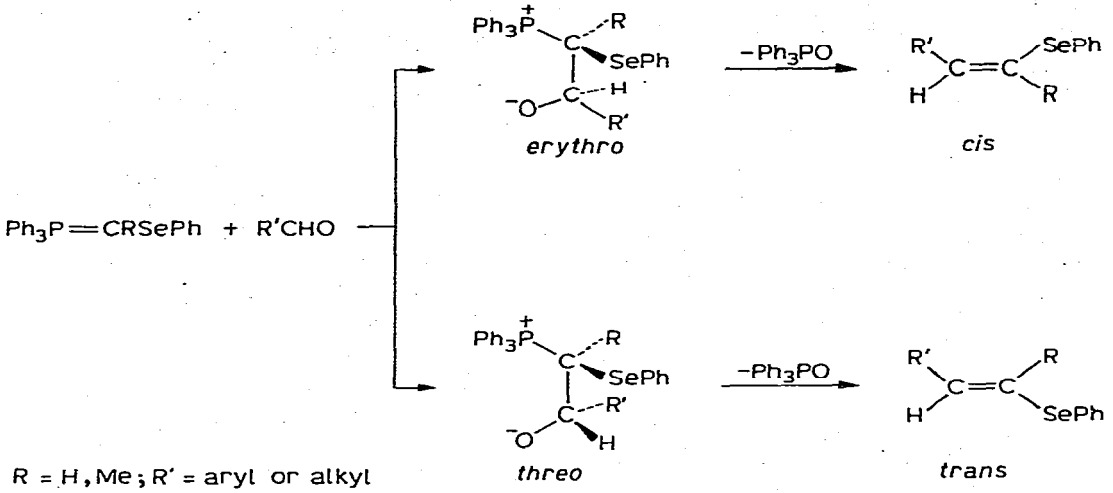

TABLE 2

RATIOS OF COMPOUNDS VII OBTAINED IN VARIOUS MEDIA

Compound	Medium	*cis*/*trans* ratio	Isomer ratio [d]
VIIa	THF	39 : 61 [a]	
VIIa	Benzene [e]	53 : 47	
VIIb	THF	36 : 64 [a]	
VIIc	THF	36 : 64 [a]	
VIId	THF	50 : 50 [b]	
VIId	Benzene [e]	25 : 75	
VIIe	THF	50 : 50 [b]	
VIIe	Benzene [e]	33 : 67	
VIIf	THF		32 : 68 [a]
VIIg	THF		38 : 62 [a]
VIIh	THF		33 : 66 [c]
VIIi	THF	50 : 50 [a]	
VIIj	THF	50 : 50 [a]	

[a] SE 30 column. [b] FFAP column. [c] By NMR. [d] See text in Results and discussion.

* An increase in the reactivity of non-stabilized or "semi-stabilized" ylides with increasing conjugation in the product olefins has been observed in earlier investigations [29,30].

Hydrolysis of vinylic selenides: ketones

Vinylic ethers [19] and thioethers [14,34] have been converted hydrolyticaly to the corresponding carbonyl compounds. We tested one of our vinylic selenide (VIIf) in order to observe if this reaction would occur for vinylic selenoethers. Employing $HgCl_2$ in CH_3CN/H_2O as the hydrolytic reagent [34] we obtained the expected ketone in 80% yield (eq. 12).

$$PhCH{=}C(CH_3)SePh \xrightarrow{CH_3CN/H_2O/HgCl_2} PhCH_2COCH_3 \qquad (12)$$

Experimental

General

Melting points were taken with a Kofler hot-plate apparatus and are uncorrected. Gas—liquid chromatography (GLC) analysis 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. NMR spectra were taken on a Varian T60 spectrometer using tetramethylsilane as an internal standard and CCl_4 or $CDCl_3$ as solvents. Infrared spectra were recorded on Perkin—Elmer 457-A or Infracord instruments. Methyltriphenylphosphonium bromide [35], ethyltriphenylphosphonium bromide [36] and selenophenol [37] were prepared by standard methods. Phenylselenenyl bromide [38] was prepared by treating diphenyl diselenide [38] with bromine.

Vinylic selenides (VII)

Reaction of selenophosphoranes with aldehydes (General procedure).

(a) Via transylidation

To a red solution of the alkylidenetriphenylphosphorane prepared from an alkyltriphenylphosphonium bromide (0.005 mol) and n-BuLi (in hexane; 0.005 mol) in 5 ml of THF, under a nitrogen atmosphere, was added dropwise with magnetic stirring at room temperature, a solution of PhSeBr (0.59 g, 0.0025 mol) in 3 ml of THF. A crystalline precipitate was formed and the color of the liquid changed to orange-yellow. After 30 min of stirring, the aldehyde was added, (pure when liquid, dissolved in 3 ml THF when solid), the mixture was refluxed for 1 h and filtered. The crystalline precipitate was identified by comparison with the authentic phosphonium salts I (R = H, CH_3, quantitative yields). The yellow solution was diluted with petroleum ether (b.p. 30—50°C, 30 ml), washed with saturated aqueous NH_4Cl and NaCl; dried with $MgSO_4$ and evaporated. The residue was dissolved in a few ml of THF and the solution treated dropwise with petroleum ether. The precipitated Ph_3PO was removed by filtration. Evaporation of the filtrate gave the crude products. Liquids were distilled (Kugelrohr) and solids were recrystallized. Analytical samples were purified by preparative TLC.

In separate runs the phosphonium salts were removed by filtering the mixture into a second reaction vessel through a curved tube charged with glass wool,

followed by addition of the aldehyde. No difference were observed in the results relative to the unfiltered reaction mixture.

(b) Starting from selenophosphonium salts

n-BuLi (in hexane, 0.0025 mol) was added dropwise to a suspension of the selenophosphonium salt IV in 5 ml of THF, at room temperature with magnetic stirring and under a nitrogen atmosphere. The aldehyde (0.0025 mol) was added to the orange solution and after 1 h at reflux, the mixture was worked up as in (a).

Two runs (to prepare compounds VIId and VIIe were performed in benzene following the same procedure. Distillation of the crude products gave butylphenylselenide as a by-product (30% by NMR). NMR spectrum (CCl_4) δ (ppm) 7.56—6.96 (5H, m, aromatic); 2.5 (2H, t, $SeCH_2$); 1.96—0.63 (7H, m, $CH_2CH_2CH_3$). The spectrum was in accordance with that of an authentic sample prepared by reaction of PhSeNa with n-bromobutane.

NMR data: see Table 3.

IR data. (liquid compounds film.: solid compounds in CCl_4). In all the compounds a strong C=C stretching frequency is observed at 1575 cm^{-1}. In compounds VIIc and VIIh the band due to this mode is covered by the broad NO_2 absorption (1570—1590 cm^{-1}). Disubstituted vinylic compounds VIIa—VIIc show a strong absorption at 945 cm^{-1} (=CH wag out of plane in the *trans* isomer [23]. This absorption is weaker in aliphatic derivatives VIId and VIIe and is completely absent in pure *cis*-VIIa [23]. For trisubstituted compounds VIIf and VIIe the frequency for this mode is shifted to 850 cm^{-1} (medium band).

(c) In salt-free media

Procedure (a) was employed using benzene as solvent and filtering before the addition of the aldehyde.

TABLE 3

NUCLEAR MAGNETIC RESONANCE DATA (δ (ppm)) OF COMPOUNDS VII

VIIa	7.61—7.1 (10H, m, aromatic); 7.1—6.43 (2H, m, CH=CH)
VIIb	8.13—7.70 (11H, m, aromatic and CH=CH) [a], 2.3 (3H, s, CH_3)
VIIc	8.33—6.40 (aromatic and CH=CH) [a]
VIId	7.56—7.03 (5H, m, aromatic); 6.56—5.76 (2H, m, CH=CH); 2.5—1.8 (2H, m, CH_2C=); 1.05 (3H, t, J 7 Hz, CH_3)
VIIe	7.56—7.03 (5H, m, aromatic); 6.56—5.33 (2H, m, CH=CH); 2.36—1.86 (2H, m, CH_2C=); 1.66—0.66 (11H, m, $CH_3(CH_2)_4$)
VIIf	7.63—7.06 (10H, m, aromatic); 6.7 (1H, b, CH=); $\frac{2.16}{2.03}$ (3H $^{d}_{d}$, $\rangle$C=C$\langle$$CH_3$)
VIIg	7.66—7.0 (9H, m, aromatic); 6.75 (1H, b, CH=); 2.28 (3H, s, $\underline{CH_3}$-Ph); $\frac{2.18}{2.05}$ (3H $^{d}_{d}$, C=CCH_3)
VIIh	8.31—7.1 (9H, m, aromatic); $\frac{6.7}{6.5}$(1H$^{b}_{b}$, CH=); $\frac{2.20}{2.06}$(3H$^{d}_{d}$, C=CCH_3)
VIIi	7.63—7.03 (5H, m, aromatic); 6.08—5.56 (1H, m, CH=); $\frac{2.56—1.76}{1.98}$ (5H $^{m,\ CH_2C=}_{d,\ C=CCH_3}$); 1.01 (3H, t, J 7 Hz, $\underline{CH_3}CH_2C(H)$=)
VIIj	7.56—7.06 (5H, m, aromatic); 6.1—5.56 (1H, m, CH=); $\frac{2.48—1.88}{1.98}$ (5H $^{m,\ CH_2C=}_{d,\ C=CCH_3}$; 1.6—0.6 (11H, m, $CH_3(CH_2)_4$)

[a] The bands are partially superimposed.

Competitive reaction of IV (R = H) with benzaldehyde and propionaldehyde

Procedure (c) was employed, treating the filtered benzene solution of IV (R = H) with a 1 : 1 mixture of PhCHO and C_2H_5CHO. The ratio of the products VIIa and VIId was determined by comparative GLC.

Phenyl(bromomethyl) selenide V (R = H)

(a) From PhSeNa and CH_2Br_2

To a suspension of NaH (1.10 g, 0.045 mol, from a 57% emulsion in oil, previously washed with hexane) in 10 mol of THF was added dropwise (nitrogen atmosphere and magnetic stirring) PhSeH (6.20 g, 0.040 mol) in 10 ml of THF. After stirring for 15 min, the resulting suspension was added dropwise to a solution of CH_2Br_2 (20 ml) in 20 ml of THF. After stirring for 1 h the mixture was filtered, and the solvent and the excess of CH_2Br_2 evaporated. Distillation of the residue (short path) gave two fractions:

Va: b.p. 97—99°C/25 mmHg; 5.0 g (50%). Found: C, 33.52; H, 2.72. C_7H_7BrSe calcd.: C, 33.63; H, 2.82%. NMR spectrum (CCl_4) δ (ppm) 7.71—7.16 (m, 5H, aromatic); 4.65 (s, 2H, CH_2)

VIa: b.p. 165°C/0.2 mmHg; 2.9 g (45%). NMR spectrum (CCl_4) δ (ppm) 4.06 (s, 2H, CH_2). IR spectrum superimposable with that of an authentic sample [21]. Similar results were obtained by refluxing the reaction mixture for 1.5 h.

(b) From PhSeBr and diazomethane

An ethereal solution of diazomethane (from Diazald * 80 ml, 0.3 *M*) and KOH was added dropwise to a solution of PhSeBr (5.0 g, 0.021 mol) in 100 ml of ether (0°C, magnetic stirring). Nitrogen evolution was observed. After stirring for 30 min at room temperature, the yellowish solution was evaporated and the residue distilled (short-path) to give Va (2.50 g, 50%), and VIa (1.6 g, 50%). Their IR and NMR spectra were identical with those of products obtained in (a).

The same reaction performed at —78°C starting from 2.36 g (0.01 mol) of PhSeBr and an equimolar amount of CH_2N_2 gave 1.90 g (80%) of pure Va.

Phenyl(1-bromoethyl)selenide (Vb)

(a) Attempts with 1,1-dihalogenoethane and PhSeNa

Attempts to prepare Vb starting from 1,1-dibromo- or 1,1-dichloro-ethane and PhSeNa (following the procedure described for Va, at room or in reflux temperature, gave only 1,1-bis(phenylseleno)ethane (VIb), b.p. 110—112°C/0.0025 mmHg, as shown by its NMR spectrum (CCl_4) δ (ppm) 7.65—7.10 (m, 10H, aromatic); 4.45 (q, 1H, *J* 7 Hz, $\underline{CH}$—CH_3); 1.8 (d, 3H, *J* 7 Hz, CH—CH_3).

(b) From PhSeBr and diazoethane

An ethereal solution of diazoethane was prepared by treating *N*-nitroso-β-ehtylaminoisobutyl methyl ketone with sodium cyclohexanoate [40]. It was titrated by reaction with benzoic acid and neutralization with NaOH [41].

* (*N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide) available by Aldrich [39].

The diazoethane solution (230 ml of 0.175 *M* solution, 0.04 mol) was added dropwise to a solution of PhSeBr (9.44 g, 0.04 mol) in 50 ml of ether, at 0°C and with magnetic stirring. Nitrogen evolution was observed.

The yellow solution was evaporated, giving 10 g (95%) of crude Vb, which was employed directly for the preparation of III. Attempts to distil the product resulted in decomposition.

NMR spectrum (CCl_4) δ (ppm) 7.70—7.05 (m, 5H, aromatic); 5.30 (q, 1H, *J* 7 Hz, CH_3—CHBr); 2.10 (d, 3H, *J* 7 Hz, CH_3—CHBr).

(Phenylseleno)methyltriphenylphosphonium bromide (III, R = H)

A solution of triphenylphosphine (11.5 g, 0.043 mol) and Va (9.0 g, 0.036 mol) in 35 ml of benzene was heated for 16 h with stirring. The crystalline product was recovered by filtration and recrystallized from CH_2Cl_2/ethyl acetate. The yield was 16.5 g (90%); m.p. 218—223°C (Found: C, 58.38; H, 4.32. $C_{25}H_{22}BrPSe$ calcd.: C, 58.61; H, 4.33%).

NMR spectrum ($CDCl_3$) δ (ppm) 8.10—6.96 (m, 20H, aromatic); 5.21 (d, 2H, *J*(PH) 7 Hz, CH_2).

1-(Phenylseleno)ethyltriphenylphosphonium bromide (III, R = CH_3) was similarly prepared from Ph_3P and Vb (80%); m.p. 184—186°C (Found: C, 59.02; H, 4.91. $C_{26}H_{24}BrPSe$ calcd.: C, 59.33; H, 4.60%).

NMR ($CDCl_3$) δ (ppm) 8.20—7.00 (m, 20H, aromatic); 6.50 (quintet, 1H, ^3J(HH) 7 Hz, CH—CH_3); 1.75 (q, 3H, ^3J(HH) 7 Hz, ^3J(PH) 20 Hz, CH—CH_3).

cis-1-Phenyl-2-phenylseleno ethylene (VIIa)

Phenylacetylene (0.50 g, 0.005 mol) was added to selenophenol (0.78 g, 0.005 mol). After 1 h at room temperature, a few ml of ethanol was added to the mixture, causing the product to crystallize. Purification was effected by recrystallization from ethanol. The yield was 1.10 g (90%), m.p. 45—47°C (lit. [24] 45—47°C). IR spectrum (CCl_4) (cm^{-1}) 905m; 998m; 1020s; 1074s; 1344m; 1445s; 1481s; 1575s (C=C stretch). In accordance with the literature [23].

NMR spectrum (CCl_4) δ (ppm) 7.60—7.10 (m, 10H); 7.10 (d, 1H, *J* 16 Hz; 6.70 (d, 1H, *J* 16 Hz), CH=CH.

Phenyl(phenylseleno)acetylene (VIII)

Phenylacetylene (1.02 g, 0.01 mol) in 5 ml THF was treated dropwise (N_2 atm., 0°C, magnetic stirring) with n-BuLi in hexane, (0.01 mol) and after 10 min with PhSeBr (2.36 g, 0.01 mol) in 4 ml of THF. The resulting yellow solution was stirred for 1 h at room temperature, and treated with saturated aqueous NH_4Cl. Petroleum ether was added (25 ml), the organic layer was washed with NaCl dried with $MgSO_4$ and evaporated. The residue was distilled (short path) giving 2.30 g (90%) of VIII: b.p. 130—137°C/0.15 mmHg (Found: C, 65.31; H, 3.90. $C_{14}H_{10}Se$ calcd.: C, 65.38; H, 3.92%). IR spectrum (film) (cm^{-1}) 2160w; 1575s; 1480s; 1440s. NMR spectrum (CCl_4) δ (ppm) 7.70—7.05 (m).

(trans)-1-Phenyl-2-phenylselenoethylene (VIIa)

Compound VIII (1.30 g, 0.005 mol) was added to $LiAlH_4$ (0.29 g, 0.0075 mol) in 7 ml of THF (room temperature, nitrogen atmosphere, magnetic stirring). The mixture was refluxed for 2 h, treated consecutively with H_2O (0.3 ml), NaOH 15% (0.3 ml), H_2O (0.9 ml). The crystalline precipitate was removed by filtration and washed with petroleum ether. The filtrate was dried with Na_2SO_4 and evaporated. The residual oil was distilled (Kugelrohr) at 100—105°C/0.05 mmHg, yield 1.20 g (92%).

The IR spectrum (film) was in accordance with literature data [23]: 945s (=C—H wag out of plane; 995m, 1020s; 1070s; 1298w (=C—H wag in plane); 1435s; 1475s; 1575s (C=C stretch). NMR spectrum (CCl_4) δ (ppm) 7.60—7.10 (m, 10H, aromatic); (6.85 (d, 1H, *J* 10 Hz), 6.65 (d, 1H, *J* 10 Hz), CH=CH).

Hydrolytic cleavage of VIIf

To a solution of VIIf (0.273 g, 0.001 mol) in 8 ml of 3 : 1 $CH_3CN \cdot H_2O$ was added $HgCl_2$ (0.55 g, 0.002 mol) in 8 ml of the same solvent mixture. The mixture was magnetically stirred at 50°C for 24 h and the crystalline precipitate removed by filtration. The filtrate was washed successively with aqueous $NaHCO_3$ and NaCl, dried with $MgSO_4$ and evaporated. The residue was distilled (Kugelrohr) at 100—115°C/25 mmHg to give 0.11 g (80%) of phenylacetone whose IR and NMR spectra were identical with those in the literature [34].

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