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Reactions of 2,5-Dihydro-2,5-Dimethoxy-Furan with Phenylselenenylchloride : Regio- and Stereocontrolled Generation of Highly Functionalized C_4 Building-Blocks

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Abstract: An efficient protocol for stereo- and regiocontrolled synthesis of small polyfunctional molecules is presented. The stereospecific addition of PhSeCl to 2,5-dihydro-2,5-dimethoxy-furan **1** in solvents, such as methylene chloride and methanol, gives cyclic and linear acetals **2** and **3**, depending on the solvent used. Emphasis is given to the regiocontrolled hydrolysis of acetal groups for the preparation of stereodefined and highly functionalized C_4 synthons, such as **8**, **9** and **13**.

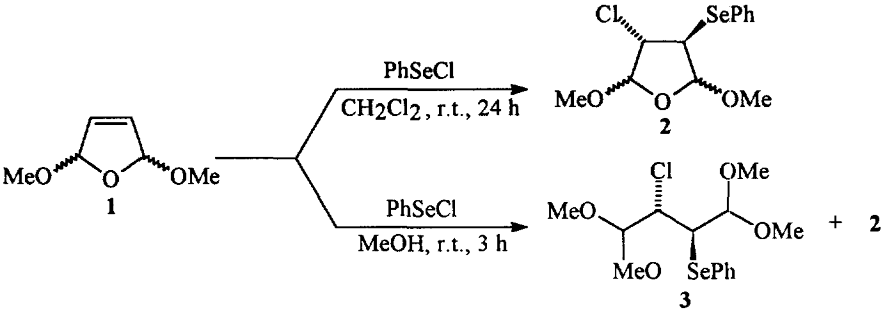
The ready availability of small and polyfunctional molecules continues to be a central goal of synthetic chemists.[1] 2,5-Dihydro-2,5-dimethoxy-furan **1** (DHDMF, a cheap and widely utilised starting material), can be considered as the synthetic equivalent of the cyclic acetal of malealdehyde, which can play a pivotal role for many synthetic purposes.[2]

Although the literature provides several important laboratory processes for the utilisation of DHDMF in organic chemistry,[3] the direct synthesis of polyfunctional C_4 blocks from **1**, though very attractive, is largely unrealised.

Stimulated by our recent outcome describing the stereospecific addition of PhSeCl to the olefinic double bond of **1**,[4] we considered the exploitation of the reactivity and synthetic utility of the addition products to be of interest, particularly with the aim of finding selective synthetic methods for the preparation of stereodefined synthons from DHDMF.

In this paper we want to report a general and valuable protocol for stereo- and regiodirected bond-forming reactions which make highly functionalized C_4 building-blocks easily accessible.

DHDMF **1** (as a *cis-trans* mixture of stereoisomers), by treatment with PhSeCl in methylene chloride for 24 h at room temperature, undergoes a stereospecific *trans* addition of the electrophile, giving clearly **2** in 70 % yield (Scheme 1).



Scheme 1

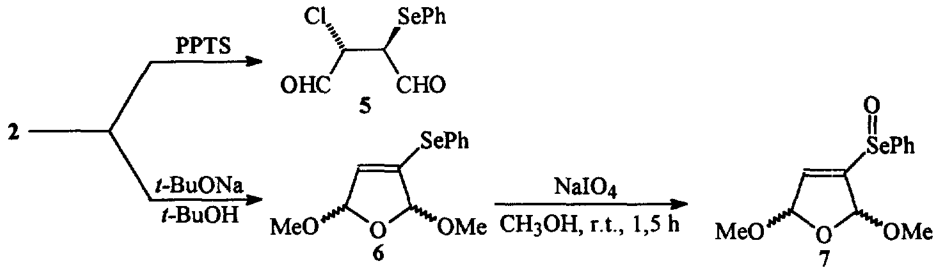
When the reaction was performed in a polar and protic solvent, such as methanol at room temperature for 3 h, the compounds **2** and **3** were obtained in a 1:2 ratio (overall yield : 70 %) (Scheme 1). Surprisingly, we did not observe the formation of phenylselenoetherification products, stemming from the nucleophilic participation of the solvent, as described in the literature.[5] The result can be explained with the hypothesis that the addition of the reagent to **1** did not involve the formation of a seleniranium cation, but a chloroselenurane as key-intermediate.[5]

A few years ago, Tiecco and co-workers described a similar result, when a considerable amount of PhCHClCHPhSePh was obtained by treatment of (*Z*)-stilbene under the same conditions.[6] A parallel experiment showed that **2** is not a precursor of **3**, since it was recovered unchanged when it was treated with PhSeCl in methanol. The outcome pointed out the unusual capability of the electrophilic reagent PhSeCl to promote the formation of fumaraldehyde bis dimethyl acetal **4** directly from DHDMF **1**.

The stereochemistry of **3** was confirmed by the following chemical correlation. The addition of PhSeCl to fumaraldehyde bis dimethyl acetal **4** (prepared by an independent way)[7] led to the stereospecific formation of the *anti*-isomer **3**.[8]

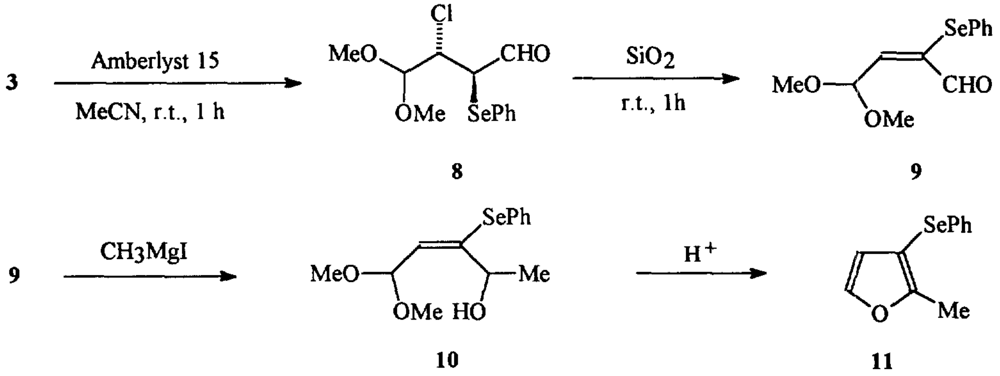
Both cyclic and linear acetals showed to be particularly useful for preparing polyfunctional C_4 synthons. In fact, the cyclic acetal **2** was smoothly deprotected by treatment with *p*-toluensolphonic acid as catalyst in acetonitrile at room temperature for 24 h, giving the dialdehyde **5** (Scheme 2), albeit in moderate yields (50 %). **5**, though unstable, was completely pure, as shown by ^{1}H-NMR data (see experimental part).

The elimination of hydrochloric acid from **2** was performed under forcing conditions, e.g., treatment with sodium *tert*-butoxide in boiling *tert*-butyl alcool : the corresponding phenyl vinyl selenide **6** was obtained in very good yields (90 %), probably through an E_{1cb} mechanism (Scheme 2). Then, the oxidation of the selenium atom in **6** with $NaIO_4$ led to the formation of the corresponding selenoxide derivative **7** in fair yields (62 %).



Scheme 2

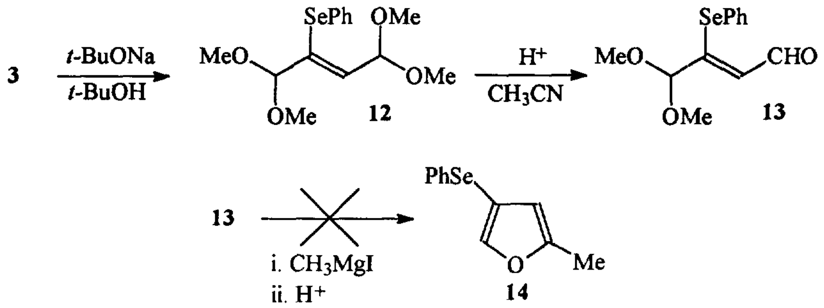
The linear acetal **3** proved to be more attractive in reaching our goal (Scheme 3).



Scheme 3

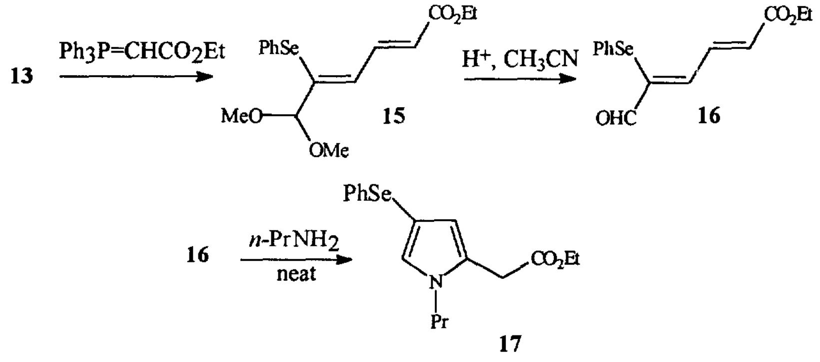
Treatment of **3** with wet Amberlyst 15 at room temperature for 1 h gave regioselectively 3-chloro-2-phenylseleno-succinaldehyde mono dimethyl acetal **8** in excellent yields (95 %). The compound **8** was obtained with a good diasteromeric excess, the ratio being determined by ^{1}H-NMR of the crude sample [9.43 (d, 1 H, *J* 3), 9.50 (d, 1 H, *J* 3), 10 :1 ratio]. However, longer reaction times decreased the diasteromeric excess ratio, since the acidic nature of the H atom at C_2 can give rise to the isomerization. The subsequent elimination of hydrochloric acid was achieved in mild experimental conditions ; the treatment of **6** with SiO_2 at room temperature for 2 h gave stereospecifically 2-phenylseleno malealdehyde mono dimethyl acetal **9** in quantitative yield. The (*E*)-stereochemistry of the olefinic double bond was determined by converting **9** into 2-methyl-3-phenylseleno-furan **11**, first by reaction of **9** with methyl magnesium iodide, and then by acidic ring closure of the secondary allylic alcohol **10** into the furan derivative **11** (Scheme 3).

On the other hand, the elimination of hydrochloric acid, carried out by treatment of **3** with sodium *tert*-butoxide in boiling *tert*-butyl alcohol, gave stereospecifically 2-phenylseleno fumaraldehyde bis dimethyl acetal **12** in quantitative yield (Scheme 4). The subsequent treatment with wet Amberlyst 15 in CH_3CN at room temperature for 2 h furnished regioselectively the pure 3-phenylseleno-fumaraldehyde mono dimethyl acetal **13** (94%).



Scheme 4

The stereochemistry of the olefinic double bond was established following the previously utilized two step sequence. The addition of CH_3MgI to the monoaldehyde **13**, followed by the acidic treatment, did not furnish the expected furan **14**, in agreement with a (*Z*)- configuration of the double bond of both compounds **12** and **13**. The vinyl phenyl selenides have become quite popular as powerful building blocks, because they serve as efficient 1,4-addition acceptors of nucleophiles.[9] The synthetic utility of the new compounds as building blocks can be shown by the following reactions sequence. The Wittig reaction, carried out on **13** with (carbethoxymethylene)triphenylphosphorane, led to the stereoselective formation of (*E,Z*)-6,6-dimethoxy-1-ethyl-5-phenylseleno-2,4-hexadienoate **15** (89%) (Scheme 5). Treatment of **15** with wet Amberlyst at room temperature for 1 h gave the corresponding aldehyde **16** (93%). The conjugated addition of a nucleophile, such as *n*-propylamine, gave rise to the subsequent intramolecular ring closure to ethyl (4-phenylseleno-1-propyl-2-pyrrolyl) acetate **17** (73%) (Scheme 5).



Scheme 5

The ready availability of simple procedures for the stereo and regiocontrolled synthesis of polyfunctionalized C_4 synthons can be considered a target of high synthetic value.

The reactivity of vinyl phenyl selenides and selenoxides as efficient Michael acceptors of nucleophiles,[9] coupled with the flexible and easily manipulated nature of the phenylselenium group,[10] make the new compounds as promising and versatile intermediates for bond-forming reactions.

EXPERIMENTAL SECTION

General procedures

^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer at room temperature with $CDCl_3$ as a solvent and as an internal standard. IR spectra were obtained with a Perkin-Elmer 457 spectrometer. Mass spectra were measured with a HP 5971 A selective mass-detector connected to a HP 5890 gas-chromatograph (electron impact : 1900 mV).

DHDMF (commercially available as a *cis-trans* mixture of stereoisomers), PhSeCl, *p*-toluensulphonic acid, Amberlyst 15 (wet), $NaIO_4$, and $Ph_3P{=}CHCO_2Et$ were utilised as purchased.

(*trans*)-3-Chloro-4-phenylseleno-2,5-dimethoxy-tetrahydrofuran (2)

PhSeCl (741 mg, 3.87 mmol) was added to a solution of DHDMF (503 mg, 3.87 mmol) in anhydrous CH_2Cl_2 (20 ml). The resulting mixture was stirred at room temperature for 24 h after which it was diluted with water and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (diethyl ether-hexane) to give the title compound **2** (902 mg, 72% yield : mixture of 4 stereoisomers ; the spectral data of the only neat-obtainable isomer are reported) as a pale yellow oil ; $\delta_H(CDCl_3)$ 3.44 (s, 3 H) 3.46 (s, 3 H) 3.67 (dd, 1 H, *J* 8.1, 4.9) 4.34 (dd, 1 H, *J* 8.1, 3.3) 5.13 (d, 1 H, *J* 4.9) 5.60 (d, 1 H, *J* 3.3) 7.2-7.4 (m, 3 H) and 7.4-7.6 (m, 2 H); $\nu_{max}(CHCl_3)/cm^{-1}$ 1201, 1109, 1098 and 1013 ; m/z 322 (M^+), 259 [M^+-(MeOH + OMe)], 227 [M^+-(OMe + CHO + Cl)] and 195 [M^+-(OMe + OMe + CHO + HCl)]. Anal. Calcd. for $C_{12}H_{15}ClO_3Se$: C, 44.81, H, 4.70. Found : C, 44.82, H, 4.62.

(*anti*)-2-Chloro-3-phenylseleno-succinaldehyde bis dimethyl acetal (3)

PhSeCl (1.47 g, 7.7 mmol) was added to a solution of DHDMF (1 g, 7.7 mmol) in methanol (40 ml).The resulting mixture was stirred at room temperature for 3 h after which it was diluted with water and extracted with diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (diethyl ether-hexane) to give first the compound **2** (595 mg, 24%) and the title compound **3** (1.303 g, 46% yield) as a pale yellow oil ; **3** : δ_H($CDCl_3$) 3.23 (s, 3 H) 3.28 (s, 3 H) 3.38 (s, 3 H) 3.44 (s, 3 H) 3.67 (dd, 1 H, *J* 8.3, 1.9) 4.35 (d, 1 H, *J* 8) 4.36 (dd, 1H, *J* 8, 1.9) 4.65 (d, 1 H, *J* 8.3) 7.2-7.4 (m, 3 H) and 7.4-7.6 (m, 2 H) ; ν_{max}($CHCl_3$)/cm^{-1} 1207, 781 754 and 673 ; m/z 368 (M^+), 305 [M^+-(MeOH + OMe)] and 258 [M^+-($C_3H_6O_2$ + HCl)]. Anal. Calcd. for $C_{14}H_{21}ClO_4Se$: C, 45.73, H, 5.75. Found : C, 45.61, H, 5.67.

(*anti*)-2-Chloro-3-phenylseleno-succinaldehyde (5)

p-Toluensulphonic acid (25 mg) was added to a solution of **2** (322 mg, 1 mmol) in 10 ml of a mixture MeCN/H_2O 5 :1. The resulting mixture was stirred for 24 h at room temperature after which it was diluted with water and extracted with diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated to give the crude title compound **5** (138 mg, 50% yield) as an unstable viscous oil which was no longer purified ; δ_H($CDCl_3$) 5.90 (dd, 1H, *J* 5.5, 1.8) 6.46 (dd, 1H, *J* 1.8, 1.5) 7.2-7.4 (m, 4 H), 7.43 (dd, 1 H, *J* 5.5, 1.5) 7.56 (m, 1 H) and 7.59 (d, 1 H, *J* 1.5) ; ν_{max}($CHCl_3$)/cm^{-1} 1780 and 1750 ; m/z 276 (M^+), 247 (M^+-CHO) and 240 (M^+- HCl). Anal. Calcd. for $C_{10}H_9ClO_2Se$: C, 43.58, H, 3.29. Found : C, 43.60, H, 3.35.

2,5-Dihydro-2,5-dimethoxy-3-phenylseleno-furan (6)

Na (30 mg, 1.3 mmol) was dissolved under magnetic stirring in 20 ml of *t*-BuOH. Then **2** (320 mg, 1 mmol) was added and the resulting mixture was stirred at 80 °C for 4 h after which it was diluted with water and extracted with diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (diethyl ether-hexane) to give the title compound **6** (256 mg, 90% yield, as a *cis / trans* mixture) as a yellow oil ; δ_H($CDCl_3$) 3.33 (s, 3 H) 3.37 (s, 3 H) 5.50 (s, 2 H) 5.56 (s, 1 H) 7.30-7.40 (m, 3 H) and 7.60-7.70 (m, 2 H) ; 3.34 (s, 3 H) 3.36 (s, 3 H) 5.50 (s, 1 H) 5.72 (d, 1 H, *J* 3.8) 5.80 (d, 1 H, *J* 3.8) 7.3-7.4 (m, 3 H) and 7.6-7.7 (m, 2 H) ; ν_{max}($CHCl_3$)/cm^{-1} 1383, 1258, 1116 and 908 ; m/z 286 (M^+), 223 [M^+-(MeOH + OMe)], 195 [M^+-(OMe + OMe + CHO)] and 129 (M^+- SePh). Anal Calcd for $C_{12}H_{14}O_3Se$: C, 50.54, H, 4.95. Found : C, 50.62, H, 4.97.

2,5-Dihydro-2,5-dimethoxy-3-phenylseleninyl-furan (7)

$NaIO_4$ (350 mg, 1.6 mmol) and $NaHCO_3$ (135 mg, 1.6 mmol) were added to a solution of **6** (143 mg, 0.5 mmol) in MeOH (10 ml) and H_2O (1.5 ml). The resulting mixture was stirred for 1.5 h at room temperature after which it was diluted with water and extracted with diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (ethyl acetate-hexane) to give the title compound 7 (94 mg, 62 % yield, as a *cis / trans* mixture) as a colourless viscous oil ; $\delta_H(CDCl_3)$ 3.28 (s, 3 H) 3.41 (s, 3 H) 5.71 (s, 1 H) 5.90 (s, 1 H) 7.03 (s, 1 H) 7.60-7.80 (m, 3 H) and 7.90-8.10 (m, 2 H) ; 3.29 (s, 3 H) 3.40 (s, 3 H) 5.97 (d, 1 H, *J* 4.1) 6.12 (d, 1 H, *J* 4.1) 7.00 (s, 1 H) 7.6-7.8 (m, 3 H) and 7.9-8.1 (m, 2 H) ; $\nu_{max}(CHCl_3)/cm^{-1}$ 1205, 1114 and 1016 ; m/z 302 (M^+), 286 (M^+- O), 223 [M^+-(MeOH + OMe + O)], 211 [M^+-(OMe + OMe + CHO)] and 145 (M^+- SePh). Anal. Calcd. for $C_{12}H_{14}O_4Se$: C, 47.85, H, 4.68. Found : C, 47.87, H, 4.77.

(*anti*)-3-Chloro-2-phenylseleno-succinaldehyde mono dimethyl acetal (8)

Amberlyst 15 (wet) (100 mg) was added to a solution of **3** (1 g, 2.7 mmol) in acetonitrile (25 ml). The resulting mixture was stirred at room temperature for 1 h, then rapidly filtered through celite and evaporated under reduced pressure to give the title compound **8** (826 mg, 95% yield) as a pale yellow oil ; $\delta_H(CDCl_3)$ 4.00 (dd, 1 H, *J* 5.9, 3) 4.68 (d, 1 H, *J* 6.1) 4.69 (dd, 1 H, *J* 6.1, 5.9) 7.2-7.4 (m, 3 H) 7.4-7.6 (m, 2 H) and 9.43 (d, 1 H, *J* 3); $\nu_{max}(CHCl_3)/cm^{-1}$ 1715 ; m/z 322 (M^+), 262 [M^+-(CHO + OMe)] and 227 [M^+-(OMe + CHO + Cl)]. Anal. Calcd. for $C_{12}H_{15}ClO_3Se$: C, 44.81, H, 4.70. Found : C, 44.92, H, 4.83.

2-Phenylseleno-malealdehyde mono dimethyl acetal (9)

Compound **8** (322 mg, 1 mmol) was adsorbed on silica gel for 1.5 h. After elution with diethyl ether and removal of the solvent under reduced pressure, the title compound **9** (283 mg, 99% yield) was obtained as a yellow oil ; $\delta_H(CDCl_3)$ 3.38 (s, 6 H) 5.33 (d, 1 H, *J* 6.2) 7.06 (d, 1 H, *J* 6.2) 7.2-7.4 (m, 3 H) 7.4-7.6 (m, 2 H) and 9.35 (s, 1 H) ; $\nu_{max}(CHCl_3)/cm^{-1}$ 1698 and 1600 ; m/z 286 (M^+), 255 (M^+- OMe) and 129 (M^+- SePh). Anal. Calcd. for $C_{12}H_{14}O_3Se$: C, 50.54, H, 4.95. Found : C, 50.55, H, 4.87.

(*E*)-5,5'-Dimethoxy-3-phenylseleno-3-penten-2-ol (10)

CH_3I (0.31 ml, 5 mmol) was added to a magnetically stirred mixture of Mg (101 mg, 5 mmol) and anhydrous diethyl ether (5 ml). After 30 minutes the mixture was cooled to -15 °C and added with a solution of **9** (286 mg, 1 mmol) in anhydrous diethyl ether by a dropping funnel. The resulting mixture was warmed to room temperature and then diluted with a saturated solution of NH_4Cl in water, until the dissolution of the precipitate was complete. After separation of the water layer, the ethereal layer was extracted with diethyl ether. The combined extracts were washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (diethyl ether-hexane) to give the title compound **10** (211 mg, 70 % yield) as a pale yellow oil ; $\delta_H(CDCl_3)$ 1.22 (d, 3 H, *J* 6) 1.90 (m, 1 H, disappears after D_2O) 3.28 (s, 3 H) 3.34 (s, 3 H) 4.04 (m, 1 H) 5.26 (d, 1 H, *J* 6) 6.27 (d, 1 H, *J* 6) 7.2-7.4 (m, 3 H) and 7.4-7.6 (m, 2 H) ; $\nu_{max}(CHCl_3)/cm^{-1}$ 3600, 3400 (large) and 1577 ; m/z 302 (M^+) and 247 (M^+- MeCHOH). Anal. Calcd. for $C_{13}H_{18}O_3Se$: C, 51.83, H, 6.02. Found : C, 51.91, H, 6.14.

2-Methyl 3-phenylseleno-furan (11)

Amberlyst 15 (wet) (30 mg) was added to a solution of **10** (301 mg, 1 mmol) in anhydrous CH_2Cl_2 (30 ml). The resulting mixture was stirred for two hours at room temperature, filtered through celite and then evaporated under reduced pressure. The residue was purified by silica gel column chromatography (diethyl ether-hexane) to give the title compound **11** (236 mg, quantitative yield) as a yellow oil ; $\delta_H(CDCl_3)$ 2.37 (s, 3 H) 6.39 (d, 1 H, *J* 2) 7.1-7.3 (m, 5 H) and 7.35 (d, 2 H, *J* 2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1510, 1235, 1012 and 759 ; m/z 238 (M^+) and 195 (M^+- $COCH_3$). Anal. Calcd. for $C_{11}H_{10}OSe$: C, 55.71, H, 4.25. Found : C, 55.69, H, 4.20.

2-Phenylseleno-fumaraldehyde bis dimethyl acetal (12)

The title compound **12** was prepared by the same procedure used for the preparation of **6**, starting from **3** (368 mg, 1 mmol); yield of **12** : 309 mg, 93%, pale yellow oil ; $\delta_H(CDCl_3)$ 3.20 (s, 6 H) 3.32 (s, 6 H) 4.55 (d, 1 H, *J* 1.0) 5.25 (d, 1 H, *J* 6.3) 6.43 (dd, 1 H, *J* 6.3, 1.0) 7.2-7.3 (m, 3 H) and 7.5-7.6 (m, 2 H) ; $\nu_{max}(CHCl_3)/cm^{-1}$ 1581, 1195, 1115 and 1055 ; m/z 332 (M^+), 253 [M^+-(C_6H_5 + 2 H)], 223 [M^+-($C_3H_7O_2$ + OMe + 3 H)] and 207 [M^+-(4 OMe + H)]. Anal. Calcd. for $C_{14}H_{20}O_4Se$: C, 50.76, H, 6.08. Found : C, 50.71, H, 6.01.

3-Phenylseleno-fumaraldehyde mono dimethyl acetal (13)

Amberlyst 15 (wet) (35 mg) was added to a solution of **12** (332 mg, 1 mmol) in acetonitrile (25 ml). The resulting mixture was stirred at room temperature for 1 h, filtered through celite and then evaporated under reduced pressure to give the title compound **13** (269 mg, 94% yield) as a yellow oil ; $\delta_H(CDCl_3)$ 3.15 (s, 6 H) 4.56 (d, 1 H, *J* 0.9) 6.91 (dd, 1 H, *J* 4.1, 0.9) 7.30-7.40 (m, 3 H) 7.60-7.70 (m, 2 H) 9.96 (d, 1 H, *J* 4.1) ; $\nu_{max}(CHCl_3)/cm^{-1}$ 1699 and 1605 ; m/z 286 (M^+), 239 [M^+-(OMe + O)] and 193 [M^+-(2 OMe + 2 H + CHO)]. Anal. Calcd. for $C_{12}H_{14}O_3Se$: C, 50.54, H, 4.95. Found : C, 50.64, H, 4.96.

(*E,Z*)-Ethyl-5-phenylseleno-6,6'-dimethoxy-2,4-hexadienoate (15)

(Carbethoxymethylene)triphenylphosphorane (334 g, 1 mmol) was added to a solution of **13** (286 mg, 1 mmol) in anhydrous benzene (10 ml). The resulting mixture was stirred at reflux temperature for 5 h under argon atmosphere, after which it was evaporated under reduced pressure. The residue was dissolved in diethyl ether and the undissolved triphenylphosphine oxide was removed by filtration; the dissolved material was precipitated by addition of petroleum ether. The mixture was then filtered and evaporated under reduced pressure to give the title compound **15** (320 mg, 89% yield) as a yellow oil; $\delta_H(CDCl_3)$ 1.30 (t, 3 H, *J* 7.1) 3.25 (s, 3 H) 3.26 (s, 3 H) 4.21 (q, 2 H, *J* 7.1) 4.70 (s, 1 H) 6.06 (d, 1 H, *J* 15.4) 6.98 (d, 1 H, *J* 11.1) 7.2-7.4 (m, 3 H) 7.4-7.6 (m, 2 H) and 7.79 (dd, 1 H, *J* 15.4, 11.1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1721, 1635 and 1106 ; m/z 356 (M^+), 278 [M^+-($C_3H_7O_2$ + 3 H)], 226 [M^+-(CH=CHCO$_2$Et + OMe)] and 200 (M^+ - SePh + H). Anal. Calcd. for $C_{16}H_{20}O_4Se$: C, 54.09, H, 5.67. Found : C, 54.08, H, 5.76.

(*E,Z*)-1-Ethyl-5-formyl-5-phenylseleno-2,4-pentadienoate (16)

The title compound **16** was prepared by the same procedure used for the preparation of **13** starting from **15** (356 mg, 1 mmol); yield of **16**: 290 mg, 93%, deep yellow oil; δ_H($CDCl_3$) 1.32 (t, 3 H, *J* 7.1) 4.25 (q, 2 H, *J* 7.1) 6.36 (d, 1 H, *J* 15.4) 7.2-7.3 (m, 3 H) 7.4-7.5 (m, 2 H) 7.53 (d, 1 H, *J* 11.2) 7.86 (dd, 1 H, *J* 15.4, 11.2) and 9.45 (s, 1 H); ν_{max}($CHCl_3$)/cm^{-1} 1720, 1695, 1406, 1277, 1248 and 1100; m/z 312 (M^+), 184 [M^+-(HC=CHCO$_2$Et + CHO)] and 155 (M^+- SePh). Anal. Calcd. for $C_{14}H_{14}O_3Se$: C, 54.38, H, 4.56. Found : C, 54.26, H, 4.50.

2-Acetic acid-ethyl ester-4-phenylseleno-N-propyl-pyrrole (17)

n-Propylamine (5 ml) was added to 60 mg (0.2 mmol) of **16**. The resulting solution was stirred at room temperature for 5 minutes, after which *n*-propylamine was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (ethyl acetate-hexane) to give the title compound **17** (51 mg, 73% yield) as a colourless oil; δ_H($CDCl_3$) 0.98 (t, 3 H, *J* 7.3) 1.23 (t, 3 H, *J* 7.2) 1.74 (m, 2 H) 3.58 (s, 2 H) 3.79 (t, 2 H, *J* 7.3) 4.14 (q, 2 H, *J* 7.2) 6.17 (d, 1 H, *J* 1.8) 6.80 (d, 1 H, *J* 1.8) and 7.0-7.3 (m, 5 H) ; ν_{max}($CHCl_3$)/cm^{-1} 1739; m/z 351 (M^+), 308 (M^+-C_3H_7), 281 (M^+- HC≡N$^+$Pr) and 194 (M^+- SePh). Anal. Calcd. for $C_{17}H_{21}NO_2Se$: C, 58.29, H, 6.04, N 4.00. Found: C, 58.40, H, 5.93, N 3.91.

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