# A Novel Push–Pull Diels–Alder Diene: Reactions of 4-Alkoxy- or 4-Phenylsulfenyl-5-chalcogene-substituted 1-Phenylpenta-2,4-dien-1-one with Electron-Deficient Dienophiles

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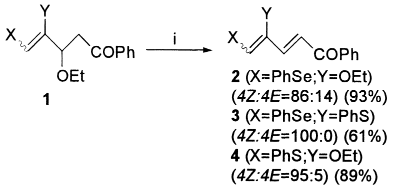
**5-(Phenylselenenyl)- and 5-(phenylsulfenyl)-4-ethoxy-1-phenyl-2,4-pentadien-1-ones (2) and (3) underwent [4+2] cycloaddition with *N*-methyl and *N*-phenylmaleimides and successive isomerization to give the 7-benzoyl-3a,4,5,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-diones 5, 8 and 9 in good yields. The 4-ethoxy group on the 2,4-pentadien-1-one was found to be effective to facilitate the cycloaddition with dienophiles. We also performed other [4+2] cycloadditions of 2,4-pentadien-1-ones with DMAD or naphthoquinone.**

**Key words** [4+2] cycloaddition; 4-alkoxy-1-phenyl-2,4-pentadien-1-one; push–pull diene; Diels–Alder reaction; selenenyl butadiene

The Diels–Alder cycloadditions of heteroatom-functionalized 1,3-butadienes have provided a powerful means to synthesize a great variety of functionalized skeletons.[1)] Alkoxy-, trimethylsilyloxy, and sulfenyl 1,3-butadienes have been commonly used as an electron-rich diene.[2,3)] On the other hand, 2,4-pentadienoates and their analogs bearing alkoxy, alkylthio or arylthio groups have been developed in novel Diels–Alder reactions, which with dienophiles highly regio- and stereoselectively give the [4+2] cycloadducts as novel precursors for natural products or bioactive compounds.[4—7)] In particular, much attention has been focused on the reactions of 5-alkoxypenta-2,4-dienoates with dienophiles bearing an electron-withdrawing group in view of the opposite regioselectivity that they show.[8,9)] However, the reactions of the push–pull dienes need strict conditions such as high pressure and high temperature.[10)] To find reactive push–pull dienes is highly important for synthetic organic chemistry. Recently, we have reported novel C–C bond formations of the 3-selenenyl-2-alkoxy-, 3-selenenyl-2-sulfenyl-, 3-sulfenyl-2-alkoxyallylic cations with phenyltrimethylsilyloxyethylene, which provided the 4-pentenophenones bearing 4- and 5-sulfenyl or selenenyl 4-alkoxy groups, in high yields.[11)] We have found that their reactions with acids or bases gave a variety of 1-phenyl-2,4-pentadien-1-ones bearing the 3-heteroatom, which are the highly reactive Diels–Alder dienes and their reactions with dienophiles were found to provide various cycloadducts. Although a small part of the results have already described in our previous report, we further investigated the Diels–Alder reactions of various dienes with dienophiles and their high reactivities were elucidated by the computational analysis. We also found the unique 1,3-hydride shift of 3a,6,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-diones obtained from the reactions with maleimides. Here we report the details of the Diels–Alder reactions of the 1-phenyl-2,4-pentadien-1-ones bearing 4-alkoxy or 4-sulfenyl group with dienophiles.

The 1-phenyl-2,4-pentadien-1-ones **2**, **3** and **4** were obtained by the treatment of 1-phenyl-4-penten-1-one **1** with NaOEt at 0 °C as shown in Chart 1. The diene **2** and **4** was a mixture of 4*Z*- and 4*E*-isomers; however, the dienes **3** was exclusively obtained as a single isomer, (2*E*,4*Z*). The stereochemistries of **2** and **4** were determined by the nuclear Overhauser effects (NOE) experiments as shown in Fig. 1. Irradiation of 4*E*-5-H increased the intensity of the methylene protons of the ethoxy group (1%). On the other hand, the NOE enhancement of the corresponding protons of 4*E*-isomer was not observed. The same results were obtained from the NOE experiments of **4**. 2- and 3-Olefinic protons were observed as the *trans* coupling constant by the $^1$H-NMR spectrum ($J$ 15 Hz). These spectral data shows the main isomer of **2** or **4** is (2*E*,4*Z*).

Next, we examined the reaction of the diene **2** (4*Z* : 4*E*=86 : 14) with *N*-phenylmaleimide to give 6-benzoyl-5-ethoxy-2-phenyl-3-(phenylselenenyl)-3a,6,7,7a-tetrahydro-1,3(2*H*)-dione (**5**) in 49% yield (Chart 2), accompanied by diphenyl diselenide, which was obtained from the thermal decomposition of **2**. The structure of **5** was determined by the spectral data, showing carbonyl absorptions at $\nu$ 1780



Reagent: i, NaOEt/EtOH/0 °C

Chart 1

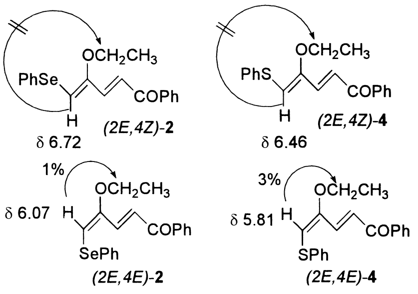


Fig. 1

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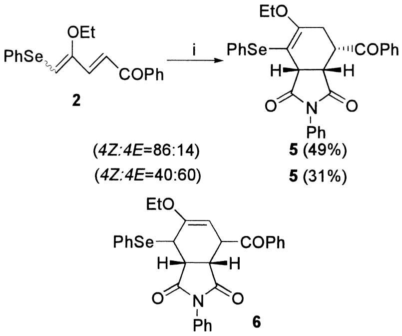
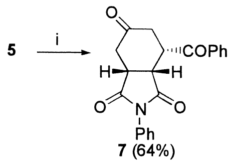


Reagent: i, *N*-phenyl maleimide/benzene/reflux/7h

Chart 2



Reagent: i, HCl/H$_2$O-EtOH

Chart 3

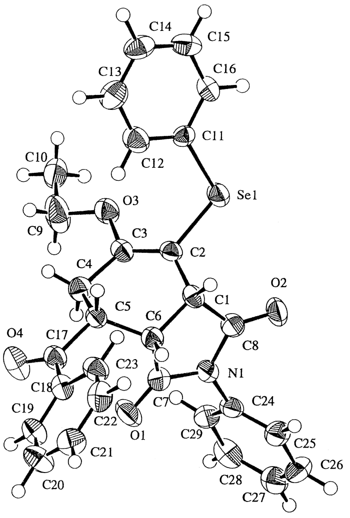
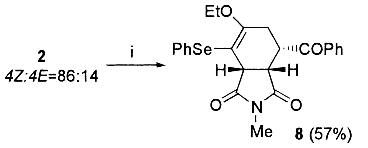


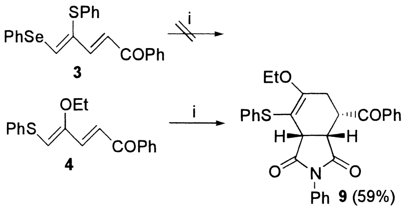
Fig. 2. ORTEP Drawing of **5**

and 1710 cm$^{-1}$ in the IR spectrum, a 5-methylene carbon at $\delta$ 25.19 ppm in the $^{13}$C-NMR spectrum, and *m/z* 531 (M$^+$) in the mass spectrum. The methine protons at 7aH, 3aH and 6H were close to each other in the $^1$H-NMR spectrum, so that we could not determine the chemical shifts and *J* values. The tetrahydroisoindole derivative **5** would not be the normal adduct **6** by its spectral data and the following experimental data as shown in Chart 3. $^{13}$C-NMR spectrum exhibited the characteristic methylene carbon of **5** at $\delta$ 25.19 ppm, which could not be observed in the spectral data of **6**. We further performed the hydrolysis of **5** using HCl/EtOH and obtained 6-benzoyl-2-phenyl-3a,4,6,7,7a-pentahydro-1*H*-isoindole-3,5(2*H*)-trione (**7**), accompanied by the successive deselenenylation of the corresponding ketone. The stereochemistry of **5** are shown in Fig. 2. The other isomers could not be observed in the NMR spectrum. The reaction of the diene **2** (4*Z*:4*E*=40:60) with *N*-phenyl maleimide under the almost same condition provided the same product **5** in 31% yield. We next performed the reaction of **2** with *N*-methyl maleimide and obtained the same-type product **8** as the *N*-phenyl derivative **5** (Chart 4). Previously, Maddaluno and coworkers fully investigated the Diels–Alder reactions of the 1-(phenylthio)-4-substituted-1,3-butadienes with maleic anhydride or maleimides and reported the photochemical [1,3] sigmatropic shift of the phenylthio group of the adducts.[12] In our case, the normal [4+2] adducts could not be observed in the reaction mixture of **2** and dienophiles. Furthermore, the product was the isoindole **5**, not the 1,3-sulfenyl migrated products. The [4+2] cycloaddition of 1-phenyl-5-sulfenyl-2,4-pentadien-1-one **4** with *N*-phenylmaleimide was examined and was found to afford the tetrahydroisoindole **9** in 59% yield (Chart 5); however, 4-sulfenyl diene **3** did not give any cycloadducts.



Reagent: i, *N*-Methylmaleimide/benzene/reflux/36h

Chart 4



Reagent: i, *N*-Phenylmaleimide/benzene/reflux

Chart 5

In order to clarify the unique isomerization, we further reinvestigated the cycloaddition reactions of **2** with *N*-phenyl maleimide and found that (2*E*,4*Z*)-1-phenyl-2,4-pentadien-1-one **2** underwent isomerization to give (2*E*,4*E*)-**2** under the reaction conditions. A benzene or CH$_2$Cl$_2$ solution of **2** (4*Z*:4*E*=86:14) and *N*-phenyl maleimide was refluxed for 2—3 h and the evaporated mixture was detected by $^1$H-NMR spectrum. The products observed were a small amount of adduct **5** and 1-phenylpenta-2,4-dien-1-one **2** (4*Z*:4*E*=1:9). This result shows that the Diels–Alder reaction of **2** would proceed after the isomerization to (2*E*,4*E*)-**2**. Therefore, we could not obtain the *concave-* or *convex-cis*-**10**, which provide the 1,3-selenenyl migrated product **11**. The reaction of (2*E*,4*E*)-**2** with dienophiles would provide the *concave* or *convex-trans*-**10**, which successively undergo 1,3-hydride shift to give the isoindole **12**. We could not explain the driving force of the 1,3-hydride shift in details; however, the benzoyl group at the 7-position of *convex-trans*-**10** would be expected to play an important role.

Next, we performed the reactions of 4-sulfenyl-5-selenenyl diene **3** with other dienophiles such as DMAD or benzoquinone and found them to provide methyl 3-benzoyl-5-phenylsulfenylphtalate (**13**) or naphthoquinone **14**, respectively (Chart 7). 5-Sulfenyl-1-phenylpenta-2,4-dien-1-one **4** also provided the ethoxyphtalate **15** or naphthoquinone **16**.

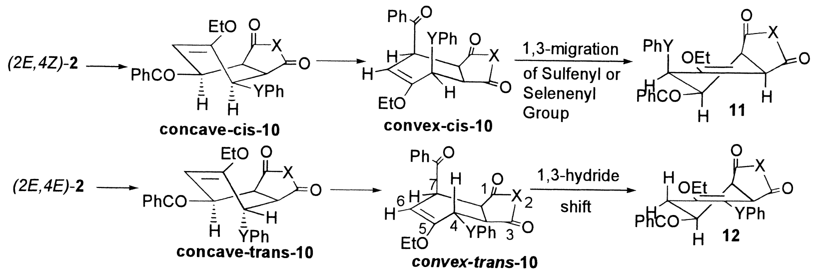
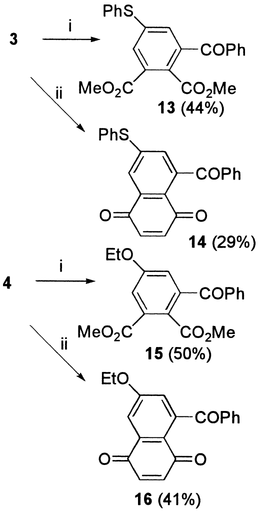


Chart 6



Reagent: i, DMAD/toluene/reflux/18h;
ii, Benzoquinone/toluene/reflux/93h

Chart 7

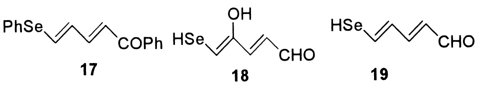


Fig. 3

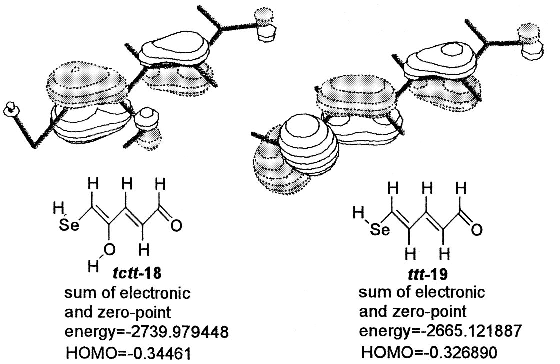


Fig. 4

Our dienes were found to be more reactive in the Diels–Alder reactions with dienophiles than the usual push–pull dienes. In order to clarify the higher reactivity of our dienes, we further investigated the reactions of 1-phenyl-5-(phenylselenenyl)-2,4-pentadien-1-one (**17**) with activated dienophiles (Fig. 3); however, the diene was recovered without formation of any adducts. These results indicate that the 4-alkoxy substituent of the penta-2,4-dienophenone **2** would play an important role.

We confirmed the results briefly by theoretical calculation of the model dienes **18** and **19**. The molecular geometries of **18** and **19** in *s-trans* forms were fully optimized at the RHF level of theory using the 6-31G* basis set and the frontier molecular orbitals (FMO) were also calculated at the same level of the theory. The results are summarized in Fig. 4. The FMO of the diene **19** mainly consists of the *n*-orbital of the SeH moiety with a small contribution of diene $\pi$-HOMO. On the other hand, in the FMO of the diene **18**, the contribution of diene $\pi$-HOMO is considerably large. The polarization of the $\pi$-HOMO of **18** toward the C5 terminus, due to the interaction with the *n*-orbital of the OH moiety on C4, is also confirmed. We propose that these features of the FMO of **18** are the major factors responsible for the enhanced reactivity, although the FMO of **18** lies slightly lower than that of **19**.

## Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Center of Instrumentation of Gifu University. $^1$H- and $^{13}$C-NMR spectra were determined of with a Varian inova 400 (400 MHz) spectrometer at Gifu University. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were determined on a JASCO IRA-100 spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained using a JEOL Gcmate spectrometer with direct-insertion probe at 70 eV. All exact mass determinations were obtained on the JMA 2000 on-line system.

**Preparation of (2*E*,4*Z*) and (2*E*,4*E*)-4-Ethoxy-1-phenyl-5-(phenylselenenyl)pent-2,4-dien-1-one (2), Typical Procedure** A EtOH (5 ml) solution of (*Z*)-3,4-diethoxy-1-phenyl-5-(phenylselenenyl)pent-4-en-1-one (**1a**) (2.74 g, 6.80 mmol) was added dropwise to a EtOH solution of EtONa (prepared from Na (0.23 g, 10.0 mmol) and EtOH (14 ml)) at 0 °C. The mixture was stirred for 15 min. The solvent was removed under reduced pressure. The mixture poured into water (100 ml), and the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layer was washed sat. NaCl solution and water, and was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt–*n*-hexane (1 : 20). (2*E*,4*Z*) and (2*E*,4*E*)-4-ethoxy-1-phenyl-5-(phenylselenenyl)pent-2,4-dien-1-one (**2**) (2.25 g, 93%) was obtained as a yellow oil. 4*Z*:4*E*=86 : 14; IR (film, cm$^{-1}$) 1680 (CO), 1180 (ether); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.44 (t, $J$=7 Hz, 4*E*-Me), 1.45 (t, $J$=7 Hz, 4*Z*-Me), 4.04 (2H, q, $J$=7 Hz, 4*E* and 4*Z*-$OCH_2$), 6.07 (s, 4*E*-olefinic H), 6.72 (s, 4*Z*-olefinic H), 7.07 (d, $J$=15 Hz, 4*Z*-olefinic H), 7.21 (d, $J$=15 Hz, 4*Z*-olefinic H), 7.30—7.59 (m, ArH and oleinic H), 7.92 (d, $J$=15 Hz, 4*E*-olefinic H), 7.95—7.99 (m, ArH, olefinic H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 16.05 (q), 67.29 (t), 99.23 (s), 119.47 (d), 124.53 (d), 128.59 (d×2), 128.82 (d×2), 129.73 (d×2), 132.93 (d), 132.96 (d×2), 136.28 (s), 138.40 (d), 152.77 (s), 190.67 (s); MS *m/z* 358 (M$^+$). *Anal.* Calcd for $C_{19}H_{18}O_2Se$: C, 63.87; H, 5.08. Found: C, 63.40; H, 5.07.

**Preparation of (2*E*,4*Z*)-1-Phenyl-5-(phenylselenenyl)-4-(phenylsulfenyl)pent-2,4-dien-1-one (3)** A tetrahydrofuran (THF) (3 ml) solution of (*Z*)-3-ethoxy-1-phenyl-5-(phenylselenenyl)-4-(phenylsulfenyl)pent-4-en-

1-one (**1b**) (0.68 g, 1.46 mmol) was added dropwise to a EtOH solution of EtONa (prepared from Na (23 mg, 1.00 mmol) and EtOH (1.00 ml)) at 0 °C. The work-up procedure provided (2*E*,4*Z*)-1-phenyl-5-(phenylselenenyl)-4-(phenylsulfenyl)pent-2,4-dien-1-one (**3**) (0.37 g, 61%) as a yellow oil. IR (KBr, cm$^{-1}$) 1680 (CO); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.19 (1H, d, 1H, $J$=14 Hz, 2-H), 7.37 (1H, d, $J$=14 Hz, 3-H), 7.15—7.61 (12H, m, ArH), 7.77—7.80 (3H, m, ArH), 8.05 (1H, d, $J$=1 Hz, olefinic H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 122.39 (d), 126.57 (d), 128.07 (d×2), 128.39 (s), 128.57 (d×2), 128.71 (d×2), 128.78 (d), 129.47 (d×2), 129.86 (d×2), 132.88 (d), 133.54 (d×2), 133.88 (s), 138.44 (s), 142.98 (d), 153.93 (d), 190.62 (s); MS *m/z* 265 (M$^+$−PhSe). *Anal.* Calcd for $C_{23}H_{18}OSSe$: C, 65.55; H, 4.31 Found: C, 65.18; H, 4.41.

**Preparation of (2*E*,4*Z*)-4-Ethoxy-1-phenyl-5-(phenylsulfenyl)pent-2,4-dien-1-one (4)** A EtOH (4 ml) solution of (*Z*)-3,4-diethoxy-5-(phenylsulfenyl)pent-4-enophenone (**2c**) (1.45 g, 4.07 mmol) was added dropwise to a EtOH solution of EtONa (prepared from Na (115 mg, 5.00 mmol) and EtOH (8 ml)) at 0 °C. The work-up procedure provided (2*E*,4*Z*)-4-ethoxy-1-phenyl-5-(phenylsulfenyl)pent-2,4-dien-1-one (**4**) (4*Z*:4*E*=95:5) (1.12 g, 89%) as a yellow oil. IR (KBr, cm$^{-1}$) 1660 (CO), 1210 (ether); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 1.45 (t, $J$=7 Hz, 4*Z*-Me), 4.02 (q, $J$=7 Hz, 4*E*-OCH$_2$), 4.07 (q, $J$=7 Hz, 4*Z*-OCH$_2$), 5.81 (s, 4*E*-olefinic H), 6.46 (s, 4*Z*-olefinic H), 7.11 (d, $J$=15 Hz, 4*Z*-olefinic H), 7.14 (d, $J$=15 Hz, 4*Z*-olefinic H), 7.19—7.59 (m, ArH), 7.93—7.99 (m, 4*E*-olefinic and ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 16.00 (q), 67.53 (t), 119.49 (d), 126.03 (d), 127.87 (d×2), 128.61 (d×2), 128.83 (d×2), 129.61 (d×2), 130.27 (d), 132.92 (d), 133.05 (s), 134.80 (s), 139.02 (d), 205.85 (s); HR-MS. Calcd for $C_{19}H_{18}O_2S$: 310.1027, found *m/z* 310.1033.

**Reaction of 2 with *N*-Phenylmaleimide** A benzene (1.50 ml) solution of **2** (4*Z*:4*E*=86:14) (100 mg, 0.28 mmol) and *N*-phenylmaleimide (0.49 g, 2.80 mmol) was heated 7 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–*n*-hexane (1:5) to give 7-benzoyl-5-ethoxy-2-phenyl-4-(phenylselenenyl)-3a,4,5,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (**5**) (73 mg, 49%) as white prisms. mp 163—167 °C (dec.); IR (KBr, cm$^{-1}$) 1780, 1710 (CO), 1210, 1130 (ether); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 1.19 (3H, t, $J$=7 Hz, Me), 2.65-2.73 (1H, m, 6-H), 2.80—2.88 (1H, m, 6-H), 3.75—3.81 (2H, m, 7- and 7a-H), 3.90 (2H, d, $J$=8 Hz, 3a-H), 3.93 (1H, q, $J$=7 Hz, OCH$_2$), 7.12—7.15 (2H, m, ArH), 7.23—7.38 (6H, m, ArH), 7.42—7.64 (5H, m, ArH), 7.85—7.87 (2H, m, ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 15.35 (q), 25.19 (t), 42.89 (d), 43.44 (d), 45.96 (d), 64.53 (t), 101.07 (s), 126.35 (d×2), 127.37 (d), 128.18 (d×2), 128.70 (d), 129.10 (d×2), 129.15 (d×2), 129.21 (d×2), 129.29 (d), 130.53 (s), 131.60 (s), 133.06 (d), 133.45 (d), 136.84 (s), 156.01 (s), 173.90 (s), 174.61 (s), 199.21 (s); MS *m/z* 531 (M$^+$). *Anal.* Calcd for $C_{29}H_{25}NO_4Se$: C, 65.66; H, 4.75; N, 2.64. Found: C, 65.11; H, 4.76; N, 2.38.

**Hydrolysis of 5 with Hydrochloric Acid** 10%HCl–H$_2$O (1.00 ml) was added dropwise to an EtOH (1.00 ml) solution of **5** (66 mg, 0.12 mmol). The mixture was refluxed for 3.5 h. The mixture was poured into water (50 ml). The work-up procedure gave 6-benzoyl-2-phenyl-3a,4,6,7,7a-pentahydro-1*H*-isoindole-1,3,5(2*H*)-trione (**7**) (32 mg, 64%) as a yellow oil. IR (film, cm$^{-1}$) 1710 (CO); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 2.78 (1H, dd, $J$=7, 19 Hz, 4-H), 2.84—2.97 (3H, m, 6-CH$_2$, 4-H), 3.47—3.56 (2H, m, 7a-H, 3a-H), 4.64—4.68 (1H, m, 7-H), 7.34 (1H, dd, $J$=1, 8 Hz, ArH), 7.38—7.44 (3H, m, ArH), 7.46—7.51 (3H, m, ArH), 7.59—7.64 (1H, m, ArH), 7.86—7.91 (2H, m, ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 37.08 (d), 37.61 (t), 40.28 (d), 40.99 (t), 42.11 (d), 126.93 (d×2), 128.88 (d×2), 129.06 (d), 129.30 (d×2), 129.47 (d×2), 132.15 (s), 134.46 (d), 134.68 (s), 176.53 (s), 177.22 (s), 200.93 (s), 205.53 (s); HR-MS. Calcd for $C_{21}H_{17}NO_4$: 347.1158, found *m/z* 347.1123.

**Reaction of 2 with *N*-Methylmaleimide** A benzene (3.00 ml) solution of **2** (0.20 g, 0.56 mmol) and *N*-methylmaleimide (0.37 g, 3.4 mmol) was heated 36 h under an Ar atmosphere. The work-up procedure provided 7-benzoyl-5-ethoxy-2-methyl-4-(phenylselenenyl)-3a,4,5,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (**8**) (140 mg, 57%) as white prisms. mp 158—162 °C (dec.); IR (KBr, cm$^{-1}$) 1780, 1700 (CO), 1220, 1100 (ether); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 1.15 (3H, t, $J$=7 Hz, Me), 2.53 (1H, ddd, $J$=2, 11, 18 Hz, 6-H), 2.74 (1H, dd, $J$=4, 18 Hz, 6-H), 2.83 (3H, s, *N*-Me), 3.62 (1H, ddd, $J$=1, 5, 9 Hz, 7a-H), 3.70 (1H, td, $J$=5, 11 Hz, 7-H), 3.77 (1H, dd, $J$=2, 9 Hz, 3a-H), 3.90 (2H, q, $J$=7 Hz, OCH$_2$), 7.22—7.30 (3H, m, ArH), 7.44—7.58 (5H, m, ArH), 7.85—7.88 (2H, m, ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 15.23 (q), 24.73 (t), 24.93 (q), 42.89 (d), 44.01 (d), 45.72 (d), 64.22 (t), 100.33 (s), 127.13 (d), 128.01 (d×2), 128.95 (d×2), 129.05 (d×2), 130.40 (s), 132.90 (d), 132.99 (d×2), 136.74 (s), 155.80 (s), 175.13 (s), 175.49 (s), 199.20 (s); MS *m/z* 469 (M$^+$). *Anal.* Calcd for $C_{24}H_{23}NO_4Se$: C, 61.54; H, 4.95; N, 2.99. Found: C, 60.88; H, 4.95; N, 2.23.

**Reaction of 4 with *N*-Phenylmaleimide** A benzene (4.00 ml) solution of **4** (0.20 g, 0.64 mmol) and *N*-phenylmaleimide (0.67 g, 3.9 mmol) was heated 25 h under an Ar atmosphere. The work-up procedure gave 6-benzoyl-4-ethoxy-2-phenyl-3-(phenylsulfenyl)-3a,4,5,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (**9**) (137 mg, 59%) as light yellow prisms. mp 148—152 °C (dec.), IR (KBr, cm$^{-1}$) 1790, 1710 (CO), 1220, 1200, 1130 (ether); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$: 1.20 (3H, t, $J$=7 Hz, Me), 2.75 (1H, dd, $J$=10, 17 Hz, 3-H), 2.82—2.88 (1H, m, 3-H), 3.75—3.85 (3H, m, 1-H, 2-H, 6-H), 3.96—4.03 (2H, m, OCH$_2$), 7.13—7.21 (3H, m, ArH), 7.23—7.42 (6H, m, ArH), 7.44—7.63 (4H, m, ArH), 7.88 (2H, dd, $J$=1, 8 Hz, ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 15.43 (q), 25.48 (t), 42.59 (d), 43.26 (d), 45.49 (d), 64.90 (t), 126.29 (d×2), 126.37 (d×2), 128.20 (d×2), 128.66 (d×2), 129.13 (d×3), 129.52 (d×2), 129.91 (s), 131.63 (s), 133.10 (d), 133.10 (d), 136.82 (s), 158.87 (s), 173.58 (s), 174.56 (s), 199.06 (s); MS *m/z* 483 (M$^+$). *Anal.* Calcd for $C_{29}H_{25}NO_4S$: C, 72.03; H, 5.21; N, 2.90. Found: C, 70.96; H, 5.25; N, 2.44.

**Reaction of (2*E*,4*Z*)-1-Phenyl-5-(phenylselenenyl)-4-(phenylsulfenyl)-pent-2,4-dien-1-one (3) and Dimethyl Acetylenedicarboxylate** A benzene (2.00 ml) solution of **3** (0.15 g, 0.35 mmol) and dimethyl acetylenedicarboxylate (0.35 g, 2.49 mmol) was heated 18 h under an Ar atmosphere. The work-up procedure gave dimethyl 3-benzoyl-5-(phenylsulfenyl)phthalate (**13**) (63 mg, 44%) as a yellow oil: IR (KBr, cm$^{-1}$) 1730, 1709 (CO); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.64 (3H, s, Me), 3.87 (3H, s, Me), 7.32—7.47 (8H, m, ArH), 7.54—7.59 (1H, m, ArH), 7.67—7.71 (2H, m ArH), 7.77 (1H, br d, $J$=2 Hz, ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 52.85 (q), 53.14 (q), 128.69 (d×2), 129.28 (d), 130.09 (d×2), 130.89 (d), 131.09 (s), 131.28 (d), 131.69 (s), 131.96 (s), 133.76 (d×2), 136.30 (s), 139.60 (s), 141.82 (s), 166.28 (s), 167.44 (s), 194.99 (s); HR-MS. Calcd for $C_{23}H_{18}O_5S$: 406.0875, found *m/z* 406.0915.

**Reaction of 3 with Benzoquinone** A toluene (2.00 ml) solution of **3** (0.15 g, 0.36 mmol) and 1,4-benzoquinone (1.27 g, 2.5 mmol) was heated 93 h under an Ar atmosphere. The work-up procedure gave 5-benzoyl-7-(phenylsulfenyl)-1,4-naphthoquinone (**14**) (38 mg, 29%) as dark yellow prisms. mp 163—166 °C; IR (KBr, cm$^{-1}$) 1717, 1672 (CO); $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$ 6.81 (1H, d, $J$=10 Hz, 3-H), 6.91 (1H, d, $J$=10 Hz, 2-H), 7.24 (1H, d, $J$=2 Hz, ArH), 7.37—7.47 (5H, m, ArH), 7.53—7.58 (3H, m, ArH), 7.64 (2H, m, ArH), 8.04 (1H, d, $J$=2 Hz, ArH); $^{13}$C-NMR (100 MHz, CDCl$_3$) 124.77 (d), 127.00 (s), 128.85 (d×2), 129.03 (s), 129.18 (d×2), 129.50 (s), 130.30 (d), 130.45 (d×2), 132.62 (s), 133.69 (d), 135.03 (d×2), 136.43 (s), 138.07 (d), 139.11 (d), 141.81 (s), 148.96 (s), 183.60 (s), 184.24 (s), 196.28 (s); HR-MS Calcd for $C_{23}H_{14}O_3S$ : 370.0663, found: *m/z* 370.0648.

**Reaction of 4 with DMAD** A toluene (2.00 ml) solution of **4** (0.15 g, 0.48 mmol) and DMAD (0.41 g, 2.90 mmol) was refluxed under an Ar atmosphere for 18 h. The work-up procedure provided dimethyl 3-benzoyl-5-ethoxyphthalate (**15**)[11] (82 mg, 50%) as a yellow oil.

**Reaction of 4 with Benzoquinone** A toluene (2.00 ml) solution of **4** (0.10 g, 0.32 mmol) and benzoquinone (0.24 g, 2.25 mmol) was refluxed under an Ar atmosphere for 15 h. The work-up procedure afforded 5-benzoyl-7-ethoxynaphthoquinone (**16**)[11] (54 mg, 41%) as purple prisms.

**X-Ray Study of 7-Benzoyl-5-ethoxy-2-phenyl-4-(phenylselenenyl)-3a,4,5,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (5)** A colorless prism was mounted on a glass fibre and transferred to the diffractometer.

Crystal data for **5**: $C_{29}H_{25}O_4NSe$ $M$=530.48, monoclinic, $a$=15.328(4) Å, $b$=9.885(2) Å, $c$=16.959(2) Å, $\beta$=110.14(1)°, $V$=2415.5(8) Å$^3$, $T$=296 K, space group $P2_1/n$, $Z$=4, $\mu$(Mo$K\alpha$)=1.593 mm$^{-1}$, $D_C$=1.460 mg m$^{-3}$. 6072 reflections collected (Rigaku AFC5R diffractometer) of which 5862 were unique (R*int*=0.077) and 2142 were observed [$I$>3.00$\sigma$($I$)]. Solved by the DIRDIF program system (ORIENT)[15] and refined by full-matrix least squares (teXsan) on $F$ of all unique data to $R$=0.044, $R_w$=0.047. CCDC 186627.

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