

Acidic work-up using 10% aqueous HCl solution gave 85% yield of cyclized *exo/endo* (60/40) mixture **1h** which was treated with acetyl iodide² to yield *cis/trans* (40/60) mixture of Douglas-Fir tussock moth pheromone **7** (27%). It was noted that *exo*-bicyclic acetal gave *trans*-pheromone and *endo* gave *cis*-pheromone selectively.² The *cis/trans* (40/60) mixture of the 6-heneicosen-11-ones turned out to be more active as a pheromone than pure material isolated from female tussock moth.¹⁸

Acknowledgment. This paper was supported by The Hallym Academy of Sciences, Hallym University and the Research Center for New Bio-Materials in Agriculture (KO-SEF).

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- Undesirable side products and non-homogeneous systems could be avoided by dilution with THF to 0.1-1.0 M in anions which were stable in THF once formed.
- Typical spectroscopic data for bicyclic acetal; *exo*-5-(*n*-bromopentyl)-7-methyl-6,8-dioxabicyclo[3.2.1]octane (**1e**) ¹H NMR (CDCl₃) δ 4.19 (q, *J*=6.4 Hz, 1H, C7-H), 4.02 (br s, 1H, C1-H), 3.39 (t, *J*=6.8 Hz, 2H), 1.9-1.39 (m, 14H), 1.16 (d, *J*=5.9 Hz, 3H, C7-CH₃); MS *m/z* 278 (M⁺+2), 276 (M⁺), 234, 232, 179, 177, 100 (base), 69, 55, 41; HRMS Calcd for C₁₂H₂₁O₂Br 276.0725, Found 276.0717.
- endo*-5-(*n*-bromopentyl)-7-methyl-6,8-dioxabicyclo[3.2.1]octane (**1e**) ¹H NMR (CDCl₃) δ 4.14 (br s, 2H, C1-H and C7-H), 3.39 (t, *J*=6.8 Hz, 2H), 1.9-1.39 (m, 14H), 1.31 (d, *J*=5.9 Hz, 3H, C7-CH₃); MS *m/z* 278 (M⁺+2), 276

(M⁺), 250, 248, 234, 232, 197, 179, 177, 155, 135, 100, 82, 69 (base), 55, 41; HRMS Calcd for C₁₂H₂₁O₂Br 276.0725, Found 276.0724.

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Convenient One-Pot Synthesis of Vinyl Selenides

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Received July 9, 1996

A number of useful functional group transformations can be achieved with vinyl selenides.¹ Owing to their ability to stabilize carbanionic intermediates for further functionalization and/or easy removal of the metalloids, they have been widely used in organic synthesis. The preparation of vinyl selenides generally implies multiple step procedures involving addition of electrophilic selenium on triple or double bonds followed by elimination reaction² or Wittig-type reactions with α -selenated ylides.^{2,15} Various vinyl selenides have been prepared by the reaction of phosphorus tetraiodide or triiodide with selenoacetals or seleno esters,²¹ the reduction of phenyl selenoalkynes,²² the reaction of alkynyl trialkyl borates,²³ alkenylboranes, and alkenyl mercurials with selenyl halides or diaryl selenides,²⁴ the addition of selenic acids²⁵ and selenols⁷ on alkynes, and the syn-elimination of selenoacetal monoselenoxides.⁸ Recently, stereoselective syntheses of (E,E)-1-arylselenobutadienes⁹ and 1-halo-1-selenoalkanes¹⁰ were also reported.

Preparation of vinyl selenides through the Horner-Emmons reaction has also been reported.⁴ But this method of using iodomethyl phosphonate and PhSeNa for starting materials needs to isolate the intermediate diethyl phenylselenomethyl phosphonate and suffers from the limited availability of starting material.

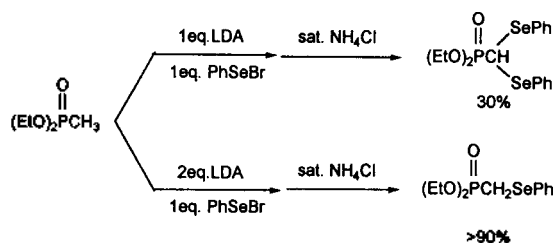
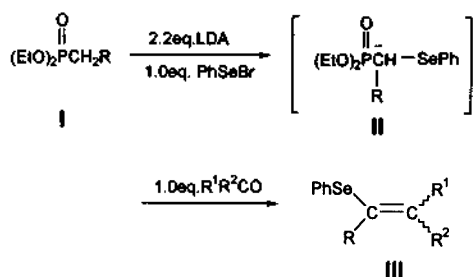
Recently, we reported the synthetic method for ketene selenoacetals^{3a} and vinyl tellurides^{3b} starting from dialkyl methylphosphonate. As an extension of these works, we here report a convenient one-pot synthesis of vinyl selenides from readily available dialkyl alkylphosphonates and PhSeBr. This method is based upon modification of Horner-Emmons reaction without isolation of its intermediate.

To obtain diethyl phenylselenomethylphosphonate, diethyl methylphosphonate was treated with PhSeBr in the presence of 1.0 equivalent of LDA. We obtained only 30% of diethyl 1,1-bis(phenylseleno)methylphosphonate probably due to the H-Li exchange reaction between diethyl lithiophosphonate and diethyl phenylselenomethyl phosphonate which was ge-

Table 1. Preparation of vinyl selenides III from diethyl alkylphosphonate I and carbonyl compounds

Entry	R	R ¹	R ²	Product	Yield (%) ^a	E/Z ratio ^b
1	H	H	Ph	PhCH=CHSePh	82	100/0
2	H	H	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄ CH=CHSePh	80	100/0
3	H	(CH ₂) ₄		=CHSePh	65	—
4	H	H	PhCH=CH	PhCH=CHCH=CHSePh	75	98/2
5	Me	H	Ph	PhCH=C(CH ₃)SePh	70	64/36
6	Me	H	CH ₃ (CH ₂) ₅	CH ₃ (CH ₂) ₅ CH=C(CH ₃)SePh	65	70/30
7	Ph	H	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄ CH=C(Ph)SePh	85	50/50

^aIsolated Yield, based on carbonyl compounds. ^bDetermined by proton NMR integration of vinylic protons.

**Scheme 1.****Scheme 2.**

nerated from reaction of diethyl lithiummethylphosphonate and PhSeBr. Using 2.0 equivalents of LDA, we could obtain diethyl phenylselenomethyl phosphonate more than 90% yields after quenching with NH₄Cl solution as shown in Scheme 1.

Synthesis of vinyl selenides has been done with a one-pot procedure by adding 1.0 equivalent of carbonyl compounds to the initially formed diethyl phenylseleno anion(II) as shown in Scheme 2. By this procedure, vinyl selenides(III) were prepared in good yields. These results are summarized in Table 1.

The use of 2.0 equivalents of LDA as a base was crucial for obtaining the desired vinyl selenides in good yields because LDA did not cause H-Li exchange reaction. When 2.0 equivalents of *n*-BuLi was used, we could obtain them less than 40% Yields. The stereoselectivity for the E isomer was observed (Entry 1, 2 and 4) as normally expected for Horner-Emmons reaction. The E/Z ratio of products was established by comparative gas liquid chromatography (GLC) with authentic samples of the E and Z isomers. The authentic samples of E-isomer were prepared by stereospecific LiAlH₄ reduction of the corresponding phenylseleno acetylene¹¹ and those of E and Z mixture were prepared by Wittig reaction.¹²

General experimental procedure is as follows: To a stirred solution of LDA, *in situ* generated from diisopropyl amine (2.2 mmol) in THF (3 mL) and a 1.6 M *n*-butyllithium solution in hexane (2.2 mmol) at -78 °C, was added diethyl alkylphosphonate (1.1 mmol) *via* syringe under nitrogen atmosphere. After being stirred for 1 h at the same temperature, phenylselenenyl bromide (1.0 mmol, in 2 mL THF) was added. After 0.5 h, carbonyl compound (1.0 mmol) was added and the reaction mixture is warmed to r.t. for 1 h. Then, sat. NH₄Cl solution (5 mL) was added and the mixture is extracted with ether (3×20 mL). The combined organic extract was dried (MgSO₄) and evaporated to give a corresponding vinyl selenide, which was purified by column chromatography on silicagel (ether/hexane=1/20) or by preparative thin layer chromatography.

In conclusion, the reaction described here represents convenient one-pot procedure for the vinyl selenides based upon modification of Horner-Emmons reaction starting from readily available diethyl alkylphosphonates(I) and carbonyl compounds.

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Photoaddition Reactions of 9,10-Phenanthrenequinone and Acenaphthenequinone to Conjugated Molecules

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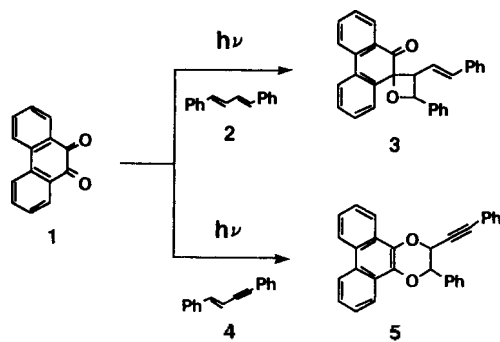
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Received July 18, 1996

Quinones are an important class of compounds in organic synthesis, in industry, and in nature.¹⁻² Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas. 9,10-Phenanthrenequinone **1** is known to add to olefins to give two types of products, keto oxetanes and 1,4-dioxins.³⁻⁵ Acetylenes also provide a useful route to synthesis of dioxole derivatives or α,β -unsaturated keto ester.⁶⁻⁷

In previous work, we have reported that 9,10-phenanthrenequinone **1** adds to *trans-trans*-1,4-diphenyl-1,3-butadiene **2** to give keto oxetane **3** as 1:1 adduct.⁸ We now report that 9,10-phenanthrenequinone **1** adds to 1,4-diphenylbut-1-en-3-yne **4** to yield 1,4-dioxin **5**, as shown in Scheme 1. In contrast, acenaphthenequinone **6** added to **2** and **4** to yield keto oxetanes, **7** and **8**, as shown in Scheme 2. The difference between the reactivities of **1** and **6** was also discussed.

Preparative photochemical reactions were conducted in a photoreactor composed of a water-cooled system and a Pyrex

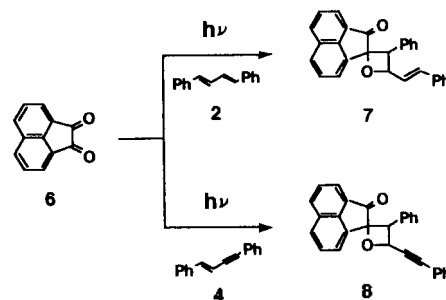


Scheme 1.

reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging the mixture with nitrogen gas (purity; 99.9%) for 30 min.

Irradiation of 208 mg (1.0 mmol) of 9,10-phenanthrenequinone **1** and 204 mg (1.0 mmol) of 1,4-diphenylbut-1-en-3-yne **4** in 100 mL of dichloromethane with 300 nm UV light for 48 h yielded 1,4-dioxin **5** in 65% yield.⁹ Photoadduct **5** was separated by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (95:5, v/v) as the eluent. Mass spectrum (EI) of **5** showed a molecular ion peak at *m/e* 412. ¹H NMR analysis of **5** revealed a 2.3:1.0 ratio of *cis*-adduct and *trans*-adduct. Two methine protons of **5** (*cis*) were observed at δ 5.63 (d, $J=2.9$ Hz) and 5.54 (d, $J=2.9$ Hz) in ¹H NMR spectra (CDCl₃), whereas those of **5** (*trans*) were found at 5.30 (d, $J=7.3$ Hz) and 5.15 (d, $J=7.3$ Hz). The H-C-C-H dihedral angles ϕ of the two isomers were obtained by using Chem 3D Plus program, in which ϕ values of **5** (*cis*) and **5** (*trans*) were 62.7° and 173.1°, respectively. The magnitude of the splitting between the two H's, i.e., $J_{\text{H,C-C-H}}$ is the largest when $\phi=0^\circ$ or 180° , and is the smallest when $\phi=90^\circ$.¹⁰ Thus, it can be considered that J_{trans} is larger than J_{cis} .

The photoadduct **3** may be formed *via* 1,4-diradical intermediate **I**, as shown in Figure 1, followed by coupling to give keto oxetane **3**.⁸ Interestingly, irradiation of **1** and **4** gave 1,4-dioxin **5**, but not keto oxetane, like **3**. This fact implies that **5** is produced by the formation of 1,4-diradical intermediate **III** and then 1,6-diradical intermediate followed by coupling to give the final product **5**. These observations are consistent with the fact that phenylpropargyl radical is more stable than phenylallyl radical, that is, radical **III** is more stable than radical **I**.¹¹ The lifetime of the more stable 1,4-radical **III** is sufficiently long to give 1,6-diradical intermediate prior to cyclization to yield 6-membered ring compound **5**. Although the alternative radical intermediates **II** and **IV** have stable benzyl radical, the evidence for the involvement of these radicals was not observed. In other words, based on the experimental results, the preferred intermediate of **3** is not **II** but **I**, and that of **5** is not **IV** but **III**. Ethynylbenzene and ethynylbenzene moieties reduce the



Scheme 2.

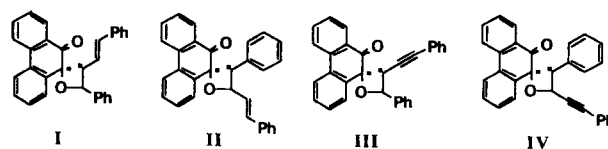


Figure 1.