

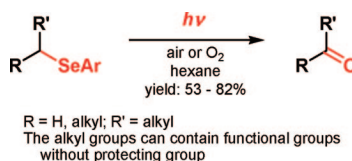
# Facile Photochemical Transformation of Alkyl Aryl Selenides to the Corresponding Carbonyl Compounds by Molecular Oxygen: Use of Selenides as Masked Carbonyl Groups

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Alkyl aryl selenides with and without functional groups on the alkyl group were transformed efficiently into the corresponding carbonyl compounds, particularly primary alkyl aryl selenides in good yields, by a simple photolysis in the presence of air or oxygen. This transformation can be conducted without protection of functional groups. The yield of carbonyl compounds was much affected by the solvent viscosity, reaction temperature, concentration of dissolved oxygen in the solvents, wavelength of light, and structure of the aryl substituents. The present study indicates that aryl selenides can be considered as a masked carbonyl group that can be easily converted to a carbonyl group by very mild reaction conditions even in the presence of various unprotected functional groups. Therefore, this functional group transformation can be used as an important tool in organic synthesis due to its simplicity and mild reaction condition.

## Introduction

Organoselenium compounds have been used as important tools in organic synthesis, and arylselenyl groups have been the most commonly used species.<sup>1</sup> Major synthetic applications of the reactions of arylselenyl compounds generally fall into two categories, i.e., C–C bond formations at the carbon atom adjacent to the selenium atom and transformations of functional groups into other functional groups. The most widely used

reactions for the C–C bond formation are those of carbanions stabilized by selenium atoms and stannyl radical-mediated reactions,<sup>1</sup> but photochemical reactions have also been reported, in which the reaction proceeds via carbon radicals that are generated by photochemical PhSe–C bond cleavages.<sup>2,3</sup> The most widely used reaction for the functional group transformation is that into olefins, which proceeds by oxidation to selenoxides and successive elimination.<sup>1</sup> Although other pho-

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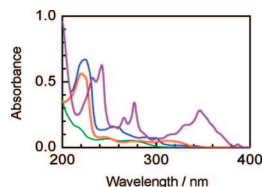
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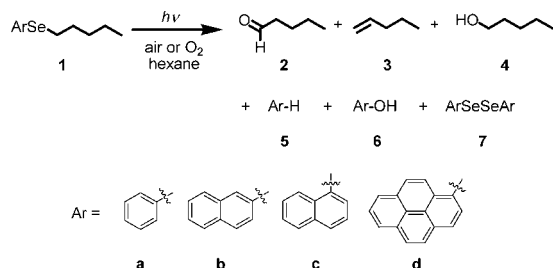
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**FIGURE 1.** Absorption spectra of **1a** (green line),<sup>10</sup> **1b** (blue line), **1c** (red line), and **1d** (purple line). Conditions: concentration,  $10^{-5}$  M in hexane; optical path length, 10 mm.

### SCHEME 1. Photolysis of Pentyl Aryl Selenides



tochemical functional group transformations into alcohols,<sup>2a,4</sup> methyl ether,<sup>2b</sup> and hydroperoxide<sup>5</sup> have been reported, simple functional group transformation into carbonyl compounds, which is more useful for synthetic purposes, has not been reported so far.

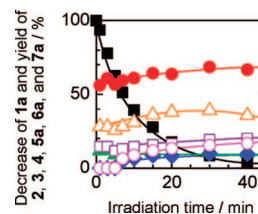
We report here a facile direct transformation of alkyl aryl selenides to the corresponding carbonyl compounds by a simple photooxidation using air or oxygen, which proceeds without the need for protection of various functional groups. This transformation can extend the scope of the utilization of arylselenenyl groups in organic synthesis and can be used as an important tool in organic synthesis.

## Results and Discussion

**Absorption Spectra of Alkyl Aryl Selenides 1.** To determine the optimal irradiation wavelength for the photolyses, the UV spectra of the pentyl aryl selenides **1** used in this study were measured. Figure 1 shows the absorption spectra of pentyl phenyl selenide (**1a**), 2-naphthyl pentyl selenide (**1b**), 1-naphthyl pentyl selenide (**1c**), and pentyl 1-pyrenyl selenide (**1d**). The UV absorption bands of **1a–d** correspond to  $\pi-\pi^*$  excitations of arylselenenyl groups<sup>6</sup> and an  $n-\pi^*$  excitation of the selenium atom.<sup>7</sup>

**Photolysis of 1a, 1b, and 1c by a Low-Pressure Mercury Lamp.** Photolysis of **1a**, **1b**, and **1c** in hexane was conducted with a low-pressure mercury lamp in air. The major products obtained were pentanal (**2**), 1-pentene (**3**), 1-pentanol (**4**), ArH compounds **5**, ArOH compounds **6**, and diaryl diselenides **7** (Scheme 1).

Figure 2 shows the results of photolysis of **1a** in hexane. Most of **1a** was consumed after 40 min of irradiation by a low-pressure mercury lamp (Figure 2), whereas the consumption was much slower for **1b** and **1c** (Figure S2, Supporting Information).<sup>8</sup> A slight increase in the yield<sup>9</sup> of the desired



**FIGURE 2.** Decrease of **1a** and yields of the photoproducts **2–7** as a function of the irradiation time. Symbols: **1a** (■), **2** (●), **3** (▲), **4** (◆), **5a** (□), **6a** (○), and **7a** (△). Photolysis conditions: concentration of **1a**, 1 mM in hexane; light source, 15 W low-pressure mercury lamp fitted with a UV-25 cutoff filter ( $0.42 \text{ mW} \cdot \text{cm}^{-2}$ ); optical path length, 10 mm; in air; room temperature. Yields of the products are based on the consumed starting material. The results are the average of three independent runs.

aldehyde **2** was observed with the progress of the photolysis for **1a**, **1b**, and **1c**, which gave a final yield of **2** of 69%, 55%, and 76% for **1a**, **1b**, and **1c**, respectively.

Scheme 2 shows a plausible reaction mechanism for the photolysis of **1**, in which the reaction in the absence of oxygen is confirmed by photolysis of **1a** under a nitrogen atmosphere.<sup>10</sup> Although details of the reaction mechanism for the formation of the oxygenated compounds **2**, **4**, and ArOH compounds **6a** and **6b** are still not clear at the moment, comparison of photolysis in the presence and in the absence of oxygen indicates clearly that these oxygenated compounds were formed by reaction(s) with oxygen, most probably via peroxy radicals. The mechanism in Scheme 2 implies that (i) facilitation of the escape of pentyl radicals from solvent cages and (ii) the increase in the ratio of path A to path B are two important factors for the increase in the yield of **2** in the photolysis.

**Solvent Effect in the Photolysis of 1a.** It is reported that the escape of pentyl radicals from solvent cages shown in Scheme 2 is facilitated by using solvents with low viscosity.<sup>10</sup> Therefore, the solvent viscosity effect on the distribution of photoproducts was studied by conducting the photolysis of **1a** in different solvents. Figure 3a shows the results for a variety of hydrocarbon solvents. As seen in the figure, the yield of oxygenated photoproducts **2**, **4**, and **6a** increased with a decrease of the solvent viscosity, which is consistent with the order of the facility of radical escape from solvent cages.

When polar solvents were used, the yield of **2** was lower than that in hydrocarbons at the same solvent viscosity (Figure 3b). This result is rationalized by the difference in the solubility of oxygen gas in the solvents; the solubility of oxygen in polar solvents is lower than that in hydrocarbons,<sup>11</sup> which reduces the probability of the reaction between oxygen and pentyl radicals. These results indicate that the photolysis should be conducted in solvents that have low viscosity and high solubility of oxygen gas to obtain **2** in high yields.

**Effect of Aryl Substituents.** The photolysis of **1a** under a nitrogen atmosphere showed the formation of **3** via abstraction of hydrogen from pentyl radicals by phenylselenenyl radicals in

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 (8) Original data are given as Supporting Information.  
 (9) Yields of the products are based on the consumed starting material.

## SCHEME 2. Plausible Reaction Mechanism for the Photolysis of Pentyl Aryl Selenides 1

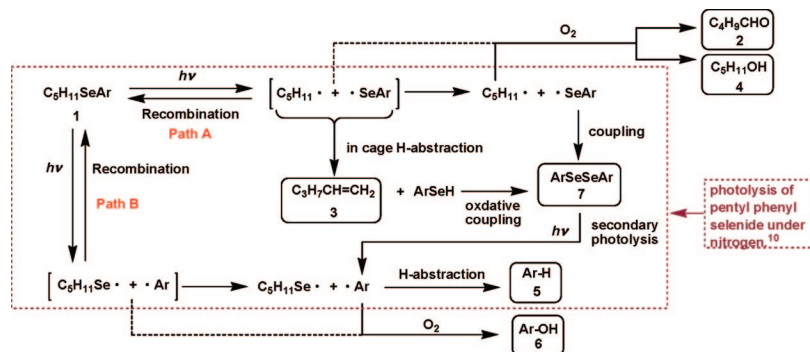
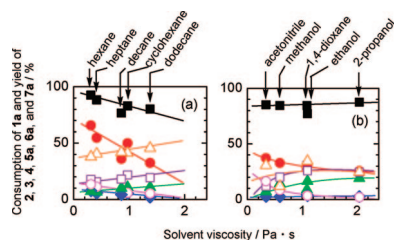


TABLE 1. Yield of 2–7 in the Photolysis of Aryl Pentyl Selenides 1

run	substrate	wavelength (nm)	irradiation time <sup>a</sup> (min)	consumption <sup>a</sup> (%)	yield <sup>a</sup> (%)							
					2	3	4	5	6	7	2 + 3 + 4	5 + 6
1	<b>1a</b>	254 <sup>b</sup>	40 (1)	95 (8)	69	13	9	24 (22)	17 (0)	36 (38)	91	41 (22)
2	<b>1b</b>		40 (5)	80 (18)	55	11	6	7 (7)	1 (0)	71 (79)	72	8 (7)
3	<b>1c</b>		40 (5)	89 (28)	76	9	7	10 (10)	2 (3)	54 (62)	92	12 (13)
4	<b>1b</b>	>330 <sup>c</sup>	40 (5)	87 (22)	63	23	10	1 (1)	0 (0)	89 (98)	96	1 (1)
5	<b>1c</b>		20 (5)	98 (29)	78	15	5	5 (5)	0 (0)	59 (79)	98	5 (5)
6	<b>1d</b>		320 (10)	98 (13)	76	13	6	8 (0)	0 (0)	54 (9)	95	8 (0)

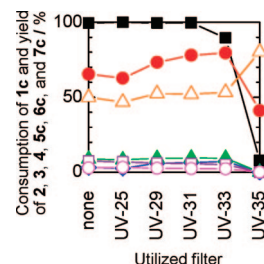
<sup>a</sup> Yields of the products are based on the consumed starting material. The results are the average of two independent runs. The values in parentheses show those at the early stage of the photolysis. <sup>b</sup> Photolysis conditions: substrate concentration, 1 mM in hexane; light source, 15 W low-pressure mercury lamp fitted with a Toshiba UV-25 cutoff filter (0.42 mW·cm<sup>-2</sup>); optical path length, 10 mm; in air; at room temperature. <sup>c</sup> Photolysis conditions: substrate, 1 mM in hexane; light source, 500 W xenon short-arc lamp fitted with an 18 cm water filter and a Toshiba UV-33 cutoff filter (0.14 mW·cm<sup>-2</sup>); optical path length, 10 mm; in air; at room temperature.



**FIGURE 3.** Consumption of **1a** and distribution of photoproducts **2–7** (a) in hydrocarbon and (b) in polar solvents as a function of the solvent viscosity. Symbols: **1a** (■), **2** (●), **3** (▲), **4** (◆), **5a** (□), **6a** (○), and **7a** (△). Photolysis conditions: concentration of **1a**, 1 mM; light source, 15 W low-pressure mercury lamp fitted with a UV-25 cutoff filter (0.42 mW·cm<sup>-2</sup>); irradiation time, 40 min; optical path length, 10 mm; in air; room temperature. Yields of the products are based on the consumed starting material. The results are the average of two independent runs.

solvent cages (cf. Scheme 2).<sup>10</sup> To suppress such hydrogen abstractions through steric hindrance of aryl groups, photolysis using the 1-naphthyl group was conducted and compared with those of phenyl and 2-naphthyl groups. Table 1, runs 1–3, shows the effect of the aryl substituents in low-pressure mercury lamp photolysis. As seen in the table, the yield of **2** from **1c** was higher than that from **1a** or **1b**, and the yield of **3** was the lowest among **1a–c**. The mass balance of the products formed by the pentyl–Se bond cleavage, **2** + **3** + **4**, was 92% for **1c**, which was comparable to that of **1a** (91%) and much higher than that of **1b** (72%). These results indicate that the 1-naphthyl group (**1c**) was the best aryl group among the three aryl substituents.

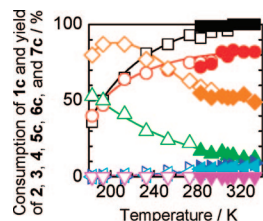
**Wavelength Dependence in the Photolysis of 1c.** The photolysis of **1a** under a nitrogen atmosphere showed that the ratio of path A in Scheme 2 increased with an increase of the irradiation wavelength.<sup>10</sup> Therefore, the wavelength effect



**FIGURE 4.** Consumption of **1c** and yield of photoproducts **2–7c** using different cutoff filters. Symbols: **1c** (■), **2** (●), **3** (▲), **4** (◆), naphthalene (**5c**; □), 1-naphthol (**6c**; ○), and bis(1-naphthyl) diselenide (**7c**; △). Photolysis conditions: concentration of **1c**, 1 mM in hexane; optical path length, 10 mm; light source, 500 W xenon short-arc lamp fitted with an 18 cm water filter and a cutoff filter; irradiation time, 20 min; in air; room temperature. Yields of the products are based on the consumed starting material. The results are the average of two independent runs.

in the photolysis of **1c**, which showed the best yield of **2** among **1a–c**, was investigated. The photolysis was conducted in hexane solutions using a xenon lamp fitted with various cutoff filters.

Figure 4 shows the wavelength effect on the photolysis of **1c** using different cutoff filters. The yield of pentanal **2** and diselenide **7c** increased with increasing irradiation wavelength<sup>8</sup> up to 330 nm (UV-33 cutoff filter). However, when longer wavelengths (UV-35 cutoff filter) were used, the yield of **2** decreased together with a drastic decrease in the consumption of **1c**; the latter can be explained by a considerable decrease in the absorption of **1c** between the light using UV-33 and UV-35 filters. From these results, irradiation using a UV-33 filter was found to be optimal for the photolysis. A similar trend was observed for **1b**,<sup>8</sup> but with slower consumption of the starting compound and lower yield of **2**.



**FIGURE 5.** Consumption of **1c** and yield of photoproducts **2–7c** as a function of the reaction temperature. Symbols: **1c** (□, ■), **2** (○, ●), **3** (△, ▲), **4** (open and solid right-pointing triangles), **5c** (open and solid left-pointing triangles), **6c** (▽, ▼), and **7c** (◇, ◆). Photolysis conditions: concentration of **1c**, 1 mM in hexane; light source, 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-33 cutoff filter ( $0.14 \text{ mW} \cdot \text{cm}^{-2}$ ); irradiation time, 20 min, optical path length, 10 mm; in air. The reaction temperature was controlled by a variable-temperature liquid nitrogen cryostat (open symbols, 183 – 313 K) or by a constant-temperature water bath (closed symbols, 293 – 333 K). Yields of the products are based on the consumed starting material. The results are the average of two independent runs.

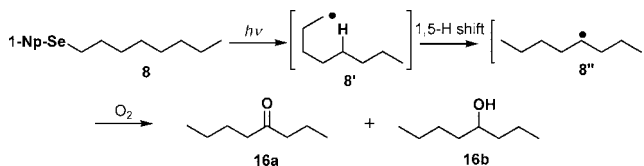
**Temperature Effect in the Photolysis of 1c.** The photolysis of **1c** was conducted at different temperatures to optimize the reaction conditions. As shown in Figure 5, the consumption of **1c** and the yield of the photoproducts were much affected by the reaction temperature. The consumption of **1c** and the yield of **2**, **4**, and **5c** increased with increased temperature, whereas the yield of **3** and **7c** decreased with increased temperature. This temperature dependence can be explained by the decrease of solvent viscosity with an increase of reaction temperature, which facilitates the escape of pentyl radicals from solvent cages (cf. Scheme 2).<sup>10</sup> This is consistent with the results obtained by experiments on the viscosity effect. However, the consumption of **1c** and the yield of **2** leveled off at about 300 K, which indicates that room temperature is optimal for the photolysis.

The optimal conditions for the photolysis of **1c** were to conduct the photolysis in hexane at room temperature using a xenon lamp fitted with a UV-33 cutoff filter. The same conditions were applied to the photolysis of **1b** and **1d**, whose time profiles of the consumption of **1** and the yields of photoproducts **2–7** were monitored.<sup>8</sup> Some of these results are summarized in Table 1, runs 4–6. As seen in the table, the rate of consumption of **1** increased in the order **1d** < **1b** < **1c**, and the yield of the desired **2** increased in the order **1b** < **1d** ≤ **1c**. The yield of **2** in the photolysis of **1b** and **1c** was increased compared with that using a low-pressure mercury lamp. The total yield of **2**, **3**, and **4** formed by the pentyl–Se bond cleavage was almost quantitative. The yield of **5** and **6** was decreased compared with that from photolysis using a low-pressure mercury lamp, particularly at the initial stage of the photolysis. This result indicates considerable suppression of the Ar–Se bond cleavage, which is consistent with significant suppression of path B in Scheme 2 using light of longer wavelength.<sup>10</sup>

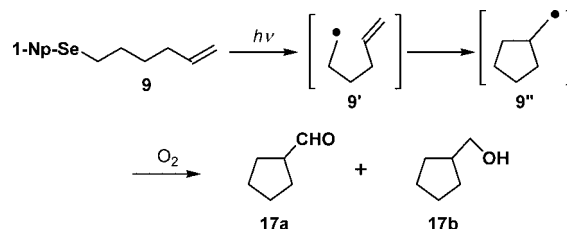
**Effect of the Oxygen Concentration in Solutions.** In the experiments on solvent effect, we have observed that the yield<sup>9</sup> of photoproducts was much affected by the amount of dissolved oxygen in solution. Therefore, to increase the yield of **2**, we have conducted the photolysis of **1b** and **1c** in air and under an oxygen atmosphere for comparison.<sup>8</sup> When the photolysis was conducted under an oxygen atmosphere instead of in air, the yield of **2** increased from 63% to 78% in the case of **1b** and from 78% to 82% for **1c**.

**Effect of the Substrate Concentration.** The effect of the substrate concentration was studied because it is preferable to conduct the reaction with a higher concentration of substrate.

### SCHEME 3. Photolysis of 8



### SCHEME 4. Photolysis of 9






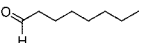


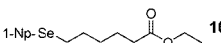
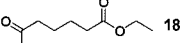
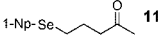
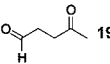


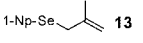

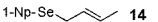


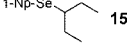

The photolysis was conducted with 10 and 20 mM hexane solutions of **1c**, both in air and under an oxygen atmosphere.<sup>8</sup> The photolysis required irradiation for a longer time with increased concentration of **1c**. When photolysis was conducted in air, the yield of the desired **2** decreased with progress of the reaction in solutions with a high concentration of **1c**, although the yield of **2** was almost the same at the initial stage of the photolysis, irrespective of the concentration of **1c**. However, when the photolysis was conducted in oxygen-saturated hexane solutions, the yield of the desired **2** in the solutions with a high concentration of **1c** was comparable to that of dilute solutions even at the final stage of the photolysis. These results indicate that the decrease of the yield of **2** at the final stage of the photolysis in air is probably due to the lack of dissolved oxygen for the reaction. This result indicates also that the same yield of **2** can be obtained in solutions with a high concentration of substrate if sufficient oxygen is supplied to the reaction mixture.

**Photolysis of Alkyl 1-Naphthyl Selenides.** Table 2 shows a summary of the photolysis of various alkyl 1-naphthyl selenides having different functional groups in the alkyl group.<sup>8</sup> The photolysis was conducted using the optimal conditions established for **1c** under an oxygen atmosphere. As seen in Table 2, the transformation to aldehydes proceeded in good yields when the alkyl group was a primary alkyl group (runs 1–5). A preparative photolysis of **10** using a larger reaction vessel with a higher concentration of substrate showed almost the same yield as that observed in the small-scale photolysis (run 4).

In the case of selenide **8**, photochemically generated terminal octyl radical **8'** may form internal octyl radical **8''** by an intramolecular 1,5-H shift because the bond dissociation energy<sup>12a</sup> of homolytic cleavage of primary C–H bonds is slightly higher than that of secondary C–H bonds (Scheme 3). From radical **8''**, formation of 4-octanone (**16a**) and 4-hydroxyoctane (**16b**) is expected from successive reaction with molecular oxygen. However, **16a** and **16b** were not detected by GLC analyses. This result indicates that it is not necessary to consider the occurrence of radical shifts within alkyl chains.

As for selenide **9**, photochemically generated hexenyl radical **9'** is known to undergo fast intramolecular exo cyclization to give cyclopentylmethyl radical **9''**,<sup>12b</sup> from which cyclopentancarboxaldehyde (**17a**) and cyclopentylmethyl alcohol (**17b**) are expected to be formed (Scheme 4). However, to our surprise, **17a** and **17b** were not detected by GLC analyses. This result indicates that oxygen trapping proceeded faster than intramolecular radical cyclization. The reason for this phenomenon is

TABLE 2. Photochemical Conversion of Alkyl 1-Naphthyl Selenides to the Corresponding Carbonyl Compounds<sup>a</sup>

Run	Substrate	Carbonyl compound	Conversion (%)	Yield (%)		
				Carbonyl compound	Olefin	Alcohol
1	1-Np-Se  <b>1c</b>	 <b>2</b>	100	80	13	7
2	1-Np-Se  <b>8</b>	 <b>16</b>	99	82	16	4
3	1-Np-Se  <b>9</b>	 <b>17</b>	96	75	19	6
4	1-Np-Se  <b>10</b>	 <b>18</b>	97 (99 <sup>c</sup> )	79 (76 <sup>c</sup> )	16	5
5	1-Np-Se  <b>11</b>	 <b>19</b>	95	74	12	1
6	1-Np-Se  <b>12</b>	 <b>20</b>	100	58	-	12
7 <sup>b</sup>	1-Np-Se  <b>13</b>	 <b>21</b>	99	61	-	13
8 <sup>b</sup>	1-Np-Se  <b>14</b>	 <b>22</b> (  <b>23</b> )	100	8 (52 <sup>d</sup> )	-	0
9	1-Np-Se  <b>15</b>	 <b>24</b>	100	53	10/32 (cis / trans)	6

<sup>a</sup> Yields of the products are based on the consumed starting material. The results are the average of two independent runs. Photolysis conditions: concentration of substrates, 1 mM in hexane; light source, 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-33 cutoff filter (0.14 mW·cm<sup>-2</sup>); irradiation time, 15 min; optical path length, 10 mm; under oxygen; room temperature. <sup>b</sup> A 1 mM concentration in heptane was used to avoid overlapping of the solvent and product peaks in GLC analysis. <sup>c</sup> Isolated yield. Photolysis conditions: concentration of **10**, 10 mM in pentane; reaction vessel, Pyrex glass test tubes (i.d. = 20 mm); light source, 500 W xenon short-arc lamp fitted with an 18 cm water filter; irradiation time, 6 h; under oxygen; room temperature. <sup>d</sup> Rearranged product **23** was obtained as a major product.

not clear at the moment, but this result indicates that we do not have to consider participation of competitive radical cyclization in the photochemical conversion of selenides to carbonyl compounds.

For selenides with primary alkyl groups, some corresponding olefins and alcohols were formed together with the desired aldehydes. The olefins were formed by abstraction of hydrogen adjacent to the carbon radical by arylselenenyl radicals within the solvent cage.<sup>10</sup> Therefore, to avoid the formation of olefins, the reaction was tested with selenides having no  $\beta$ -hydrogen atoms to the selenium atom (runs 6 and 7), in which the formation of olefins is not possible. To our surprise, the yield of the corresponding aldehydes was slightly lower than those of primary alkyl groups despite the fact that a significant side reaction, formation of olefins, was completely blocked.

Although 2-methylallyl selenide **13** gave corresponding aldehyde **21** in a good yield (run 7), allylic radicals are known to react at both its ends. Therefore, the reactivity of unsymmetrical allylic radical was tested using *trans*-2-butenyl selenide **14**; the yield of the expected *trans*-2-butenal (**22**) was low and showed a preferential formation of methyl vinyl ketone (**23**) (run 8). This result indicates that, in the case of unsymmetrical allylic radicals, the carbonyl group is preferentially introduced at the more substituted end of the allylic radicals.

The yield of ketone from the secondary alkyl group was lower than that of the primary alkyl group due to formation of a

considerable amount of olefins, which is most probably due to the larger number of hydrogen atoms on the carbons adjacent to the carbon radical, which increases the probability of hydrogen abstraction to form olefins.

## Conclusion

Alkyl aryl selenides with and without functional groups on the alkyl group were transformed efficiently into the corresponding carbonyl compounds, particularly primary alkyl aryl selenides in good yields, by a simple photolysis in the presence of air or oxygen. The yield of carbonyl compounds was much affected by the solvent viscosity, reaction temperature, concentration of dissolved oxygen in the solvents, wavelength of light, and structure of the aryl substituents. The best photolysis condition was to conduct the photolysis in hexane at room temperature under an oxygen atmosphere using a 1-naphthyl group as an aryl group with a xenon lamp fitted with a UV-33 cutoff filter. The present study indicates that aryl selenides can be considered as a masked carbonyl group that can be easily converted to a carbonyl group by very mild reaction conditions even in the presence of various unprotected functional groups. Therefore, this functional group transformation can be used as an important tool in organic synthesis due to its simplicity and mild reaction conditions.

## Experimental Section

**General Aspects.** Selenides **1a–d** and **8–15**, diselenides **7c** and **7d**, aldehydes **17–19**, and olefins **29** and **31** were synthesized by general procedures.<sup>8</sup> The solvents used for the photolyses were spectral grade methanol, ethanol, 2-propanol, acetonitrile, and 1,4-dioxane, guaranteed reagent grade heptane, decane, dodecane, and cyclohexane, and fractionally distilled spectral grade hexane. Authentic samples of **2**, octanal (**16**), benzaldehyde (**20**), 2-methyl-2-propenal (**21**), **22**, **23**, 3-pentanone (**24**), **16a**, **17a**, pentanol, octanol, 5-hexenol, ethyl 6-hydroxyhexanoate, 4-oxopentanol, benzyl alcohol, 2-methyl-2-propenol, 3-buten-2-ol, *trans*-2-butenol, 3-pentanol, **16b**, **17b**, 1-pentene, 1-octene, 1,5-hexadiene, *trans*-2-pentene, *cis*-2-pentene, benzene, naphthalene, pyrene, phenol, 1-naphthol, 2-naphthol, and pentane were purchased and used as received.

**Photolysis of Alkyl Aryl Selenides.** The photolysis was conducted in 1.5 mL of solution in air or under an oxygen atmosphere using a synthetic quartz cell of 10 mm width and 10 mm optical path length fitted with a Teflon/silicon rubber septum. The solutions for the photolysis of **1a–d** and **8–15** (1 mM) were saturated with air or with oxygen before photolysis. *Caution: general precautions have to be taken for handling pure oxygen, and it is desirable to put a safety glass in front of the reaction vessel!* The photolysis was conducted with a 500 W xenon lamp fitted with an 18 cm water filter and a cutoff filter (UV-29, UV-31, UV-33, or UV-35) or with a 15 W low-pressure mercury lamp fitted with a UV-25 cutoff filter. In the experiments on the temperature effect, the temperature was controlled by a variable-temperature liquid nitrogen cryostat (183–313 K) or by a constant-temperature water bath fitted with a recirculating chiller (293–333 K). The light intensity of the xenon lamp was measured by a spectroradiometer. The consumption of **1** and the yield of product were analyzed by comparison with authentic samples by capillary GLC [capillary columns, NEUTRA BOND-1 (60 m, 0.25 mm i.d., 1.5  $\mu$ m thickness) or INERT CAP-1 (30 m, 0.25 mm i.d., 1.5  $\mu$ m thickness)] and HPLC [RP-8e column (250 mm, 4 mm i.d.)] fitted with a UV detector (detected at 254 nm). For all GLC and HPLC analyses, absolute yields of products were determined using standard

solutions of authentic samples, and the yields of each product were calculated from the following equation:  $100 \times [\text{absolute yield (\%)}] / [\text{consumption of starting materials (\%)}]$ .

**Preparative Photolysis of 5-(Ethoxycarbonyl)pentyl 1-Naphthyl Selenide (10).** A 20 mL sample of an oxygen-saturated hexane solution of **10** [10 mM, 70 mg (0.2 mmol)] was transferred into two 20 mL Pyrex test tubes (i.d. 20 mm) fitted with silicon rubber septa that were connected to a balloon filled with oxygen with syringe needles. *Caution: general precautions have to be taken for handling pure oxygen, and it is desirable to put a safety glass in front of the reaction vessel!* The photolysis was conducted for 6 h with a 500 W xenon lamp fitted with an 18 cm water filter. The solvent was evaporated in vacuo, and the crude products were purified by silica gel column chromatography (*n*-hexane:ethyl acetate = 50:1), yielding 24 mg (76%) of the desired aldehyde **18** as a colorless oil. <sup>1</sup>H NMR ( $\delta$ ): 1.26 (3H, t, *J* = 7.2 Hz), 1.62–1.70 (4H, m), 2.27–2.36 (2H, m), 2.43–2.50 (2H, m), 4.08–4.16 (2H, q, *J* = 7.2 Hz), 9.76 (1H, s) ppm. <sup>13</sup>C NMR ( $\delta$ ): 14.2, 21.5, 24.4, 34.0, 43.5, 60.4, 173.2, 202.0 ppm. GLC analysis showed that the product was identical to an authentic sample of **18**.

**Supporting Information Available:** Synthetic procedure of alkyl aryl selenides **1a–d**, **8–15**, diselenides **7c** and **7d**, aldehydes **17–19**, and olefins **29** and **31**, results on the consumption of **1b** and **1c** and yield of photoproducts using a low-pressure Hg lamp (UV-25 cutoff filter), consumption of **1b** and yield of photoproducts using a Xe lamp (different cutoff filters), consumption of **1b–d** and **8–15** and yield of photoproducts using a Xe lamp (UV-33 cutoff filter), and consumption of **1c** and yield of photoproducts (with high substrate concentration in air and under an oxygen atmosphere) using a Xe lamp (UV-33 cutoff filter), and emission spectra of a xenon lamp fitted with an 18 cm water filter and different cutoff filters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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