

# Sunlight Oxidation of Alkyl Aryl Tellurides to the Corresponding Carbonyl Compounds: A New Carbonyl Precursor

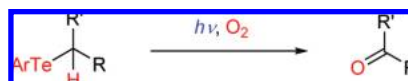
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## ABSTRACT

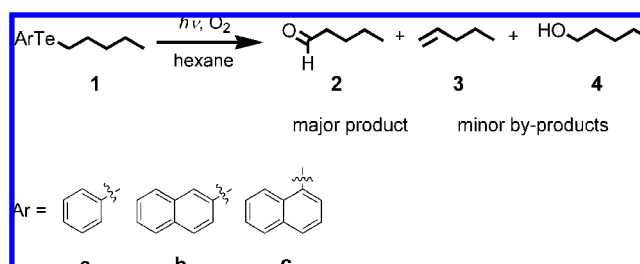


Alkyl aryl tellurides were efficiently transformed to the corresponding carbonyl compounds by photo-oxidation with sunlight without affecting various functional groups in the alkyl moiety. The tellurides can be used as a new carbonyl precursor, and the photolysis can be conducted without special equipment for light sources.

Carbonyl groups play an important role in the synthesis of organic molecules, thus various precursors have been developed to introduce the carbonyl moiety at a particular stage in the synthesis.<sup>1</sup> However, many functional groups in the molecule are affected by the reaction conditions when converting precursors to carbonyl groups; therefore, protection–deprotection of the functional groups is frequently required for the conversion. We report here a new carbonyl precursor, the easily accessible alkyl aryl telluride,<sup>2</sup> that can be transformed to the corresponding carbonyl group by a simple photo-oxidation, even using sunlight, without affecting other functional groups in the molecule. Although various photochemical reactions of organic tellurides have been reported,<sup>3–5</sup> the efficient conversion of tellurides to carbonyl groups has not been reported.

Optimization of the photochemical transformation was conducted with aryl pentyl tellurides **1a–c** (Scheme 1); pentanal (**2**) was obtained as a major product together with

Scheme 1. Photolysis of Aryl Pentyl Tellurides **1a–c**



minor byproduct 1-pentene (**3**) and 1-pentanol (**4**) (vide infra). Figure 1 shows the absorption spectra of **1a–c**. As seen in the figure, **1a–c** have considerable absorption over 330 nm, particularly **1b,c**. The absorption over 330 nm can be assigned to the n– $\sigma^*$  transition of the Te–C bond,<sup>6</sup> which is supported by a DFT calculation.<sup>7</sup>

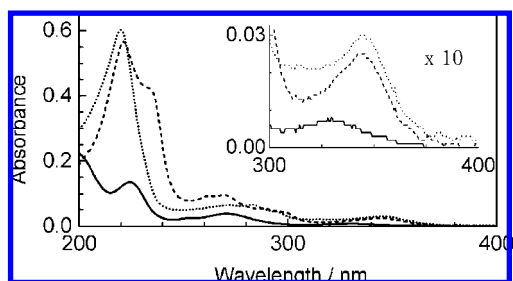
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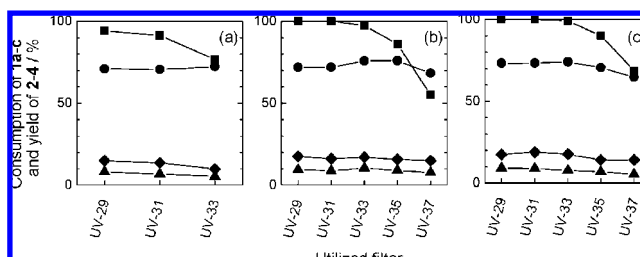
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**Figure 1.** Absorption spectra of *n*-pentyl phenyl telluride (**1a**, solid line), 2-naphthyl *n*-pentyl telluride (**1b**, broken line), and 1-naphthyl *n*-pentyl telluride (**1c**, dotted line). Concentration =  $10^{-5}$  M in *n*-hexane, optical path = 10 mm.

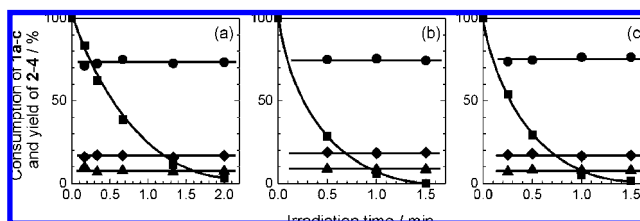
Figure 2 shows the results of the effect of wavelength and aryl group on the photolysis. The photolyses were conducted in hexane under an oxygen atmosphere with a xenon lamp fitted with different cutoff filters; the photoproducts were assigned and quantified by GC analyses in comparison with authentic samples.<sup>8</sup> Figure 2 shows that the consumption of **1a–c** decreased with increased wavelength of the irradiated light, which can be explained by a decrease in the absorption of light (cf. Figure 1). In contrast, the yield of **2** showed a small maximum when a UV-33 filter was used, where the yield did not depend on the structure of the aryl group. These results indicated that irradiation using a UV-33 filter was the optimal condition to obtain the best balance between the rate of photolysis and the yield of product.

The effect of irradiation time was investigated using a xenon lamp with a UV-33 filter (Figure 3). For tellurides **1a–c**, the reaction was complete within 2 min with a similar yield of **2**. The rate of photolysis was more than 10-fold faster than the selenium analogue,<sup>10</sup> which was most probably due to the smaller bond energy of the C–Te bonds



**Figure 2.** Consumption of (a) **1a**, (b) **1b**, (c) **1c**, and yield of photoproducts using different cutoff filters.<sup>8,9</sup> Symbols: aryl pentyl telluride (**1a–c**, ■), pentanal (**2**, ●), 1-pentene (**3**, ▲), and pentanol (**4**, ◆). Concentration of **1a–c** = 1 mM in hexane, light source = 500 W xenon short-arc lamp fitted with an 18 cm water filter ( $17.5 \text{ mW}\cdot\text{cm}^{-2}$ ) and a cutoff filter, irradiation time = 1 min, reaction vessel = quartz cell (optical path = 10 mm), oxygen atm, rt. Wavelength of light, UV-29 = >290 nm; UV-31 = >310 nm; UV-33 = >330 nm; UV-35 = >350 nm; UV-37 = >370 nm.

compared with that of the C–Se bonds.<sup>11</sup> Besides products **2–4** that were generated from pentyl moiety, ArH, ArOH, and ArTeTeAr were formed from aryl moieties with the total yield of 75–85%.<sup>8</sup> For comparison, photolyses of 1- and 2-naphthyl pentyl sulfides were conducted;<sup>8</sup> however, the rate of the reaction was more than 50-fold slower and the yield of **2** was less than 20%.



**Figure 3.** Consumption of (a) **1a**, (b) **1b**, (c) **1c**, and yield of photoproducts as a function of irradiation time.<sup>9</sup> Symbols: aryl pentyl telluride (**1a–c**, ■), pentanal (**2**, ●), 1-pentene (**3**, ▲), and pentanol (**4**, ◆). Concentration of **1a–c** = 1 mM in hexane, light source = 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-33 filter ( $14.7 \text{ mW}\cdot\text{cm}^{-2}$ ), reaction vessel = quartz cell (optical path = 10 mm), oxygen atm, rt.

In analogy with the reaction mechanism of pentyl phenyl selenide,<sup>10,12</sup> products **2–4** were expected to be formed via carbon radicals that were generated by photochemical alkyl–Te bond cleavage.<sup>5</sup> The pentyl group was quantitatively transformed to products **2–4**, which was confirmed by the sum of the three products equaling 100%. The yield of **2** was not affected by the difference in the aryl group but showed a slight difference in the rate of the reaction and the

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(8) Original data and/or experimental details are given as Supporting Information.


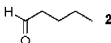
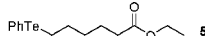
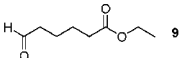

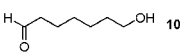

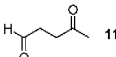
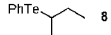

(9) Yields of the products are based on the consumed starting material. The results are the average of at least two independent runs.

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**Table 1.** Photochemical Transformation of Alkyl Phenyl Tellurides to the Corresponding Carbonyl Compounds

run	substrate	product	solvent	photolysis condition <sup>a</sup>	conversion/ %	yield <sup>b</sup> / %
1			hexane	Xe lamp <sup>c</sup>	96	75
2			benzene	Xe lamp <sup>c</sup>	97	46
3			toluene	Xe lamp <sup>c</sup>	92	61
4			CH <sub>2</sub> Cl <sub>2</sub>	Xe lamp <sup>c</sup>	92	49
5			THF	Xe lamp <sup>c</sup>	96	55
6			hexane	sunlight (sunny) <sup>e</sup>	98	76
7			hexane	sunlight (cloudy) <sup>e</sup>	78	76
8			hexane	Xe lamp <sup>c</sup>	98	76 (73) <sup>d</sup>
9			hexane	sunlight (sunny) <sup>e</sup>	99	74
10			hexane	Xe lamp <sup>c</sup>	97	72 (72) <sup>d</sup>
11			hexane	sunlight (sunny) <sup>e</sup>	99	71
12			hexane	Xe lamp <sup>c</sup>	99	73
13			hexane	sunlight (sunny) <sup>e</sup>	97	72
14			hexane	sunlight (cloudy) <sup>e</sup>	81	74
15			hexane	Xe lamp <sup>c</sup>	100	48
16			hexane	sunlight (sunny) <sup>e</sup>	100	46

<sup>a</sup> Conducted in hexane solutions under an oxygen atm at rt. <sup>b</sup> Yields of the products are based on the consumed starting material and determined by GC analyses. The results are the average of two independent runs. <sup>c</sup> Photolysis condition: concn of substrates = 1 mM, light source = 500 W Xe lamp fitted with a UV-33 filter (14.7 mW·cm<sup>-2</sup>), irradiation time = 2 min, reaction vessel = quartz cell. <sup>d</sup> Isolated yield. Photolysis condition: concn of substrates = 10 mM, light source = 500 W Xe lamp (17.5 mW·cm<sup>-2</sup>), irradiation time = 90 min, reaction vessel = Pyrex round-bottomed flask. <sup>e</sup> Photolysis condition: concn of substrates = 1 mM, light source = sunlight (ref 8), irradiation time = 10 min, reaction vessel = Pyrex round-bottomed flask.

distribution of byproducts **3** and **4**. The rate of photolysis was about 1.4-fold faster for **1b,c** than for **1a**. However, the phenyl group rather than 1- and 2-naphthyl groups was selected for further study because of the easy accessibility of diphenyl ditelluride which was used for the preparation of alkyl aryl tellurides **1**.

Before further investigation on the photo-oxidation of various tellurides was carried out, their thermal stability was tested using telluride **8**. Telluride **8** was quantitatively recovered after 3 h of reflux in hexane under air in the dark, which indicated that the tellurides had sufficient thermal stability. In addition, photochemical stability in the laboratory environment was tested using **1c**; a hexane solution of **1c** (1 mM) in a quartz cell was placed under six 32 W fluorescent lamps (about 2 m from two and 3 m from four lamps), which showed quantitative recovery of **1c** even after 4 h. These results indicate that tellurides can be handled without precaution in low light or temperature.

Table 1 shows the results with different alkyl groups.<sup>8</sup> Runs 1–5, 8, 10, 12, and 15 were conducted with a xenon lamp fitted with a UV-33 filter. As shown in the table, the photolyses were almost complete within 2 min. Runs 1–5 show that highest yield was obtained when hexane was used as a solvent. The yields of the corresponding aldehydes **2** and **9–11** obtained from primary alkyl groups were almost the same in hexane (runs 1, 8, 10, and 12). However, the yield of ketone **12** from secondary alkyl telluride **8** was lower

than those of the aldehydes, which was due to a considerable increase in the formation of olefins (*cis*- and *trans*-2-pentene: 10 and 30%, respectively). It should be noted that the protection of functional groups was not necessary during the photolysis. This was accomplished by using long-wavelength light for the photolysis, which prevented secondary photolysis by avoiding absorption of light by the functional groups including the generated carbonyl groups.

Runs 8 and 10 also show the isolated yields of the products. The photolyses were conducted with a higher substrate concentration and longer irradiation time with a xenon lamp using a Pyrex round-bottomed flask. A UV-33 filter was not used when the Pyrex flask was utilized for photolysis because Pyrex glass has a similar function to the cutoff filter. As seen in the table, the isolated yields of the carbonyl compounds **9** and **10** were the same as those obtained by the xenon lamp photolysis determined by GC analyses.

As the tellurides showed high photoreactivity, we investigated the use of sunlight for photolysis. Solar photochemical reactions have recently attracted much attention of researchers in the field of green chemistry.<sup>13</sup> Runs 6, 9, 11, 13, and 16 show the results of sunlight photolysis on sunny days.<sup>8</sup> The photolysis was conducted using a Pyrex round-bottomed flask without cutoff filters. As shown in Table 1, the photo-oxidation was almost complete after 10 min irradiation and gave the same yield of products as that after 2 min xenon

lamp irradiation. When sunlight photolysis was conducted on cloudy days (runs 7 and 14), the yield of the carbonyl compounds remained the same but the conversion of the starting tellurides was less than that on sunny days.

In conclusion, alkyl aryl tellurides with and without functional groups on the alkyl moiety were efficiently transformed into the corresponding carbonyl compounds, particularly to aldehydes, in good yields. These results indicate that aryltelluro groups can be used as a precursor to carbonyl groups. The transformation was accomplished by simple irradiation with light under oxygen without affecting various unprotected functional groups in the molecules. The photolysis also proceeded effectively with

sunlight irradiation, which implies that the reaction can be performed without special equipment for light sources.

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**Supporting Information Available:** Experimental procedures and full spectroscopic data. Absorption spectra of 1- and 2-naphthyl pentyl sulfides. Emission spectra of a xenon short-arc lamp fitted with different cutoff filters, and that of sunlight. Consumption of 1- and 2-naphthyl pentyl sulfide and yield of photoproducts using a Xe lamp (different cutoff filters). Consumption of 1- and 2-naphthyl pentyl sulfide and yield of photoproducts as a function of irradiation time using a Xe lamp. The yield of photoproducts in the photolysis of alkyl aryl tellurides (**1a–c**) and alkyl aryl sulfides. Intensity of sunlight in the photolysis. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1a–c**, **5–8**, **10**, **13**, **14**, bis(1-naphthyl)ditelluride, bis(2-naphthyl)ditelluride and sulfide, and 2-methyl-2-[3-(phenyltelluro)propyl]-1,3-dioxolane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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