

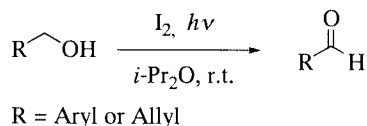
## New Synthetic Method of Benzaldehydes and $\alpha,\beta$ -Unsaturated Aldehydes with $I_2$ under Photoirradiation

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Benzylic alcohols and allylic alcohols were found to be oxidized to the corresponding benzaldehydes and  $\alpha,\beta$ -unsaturated aldehydes easily in the presence of  $I_2$  under photoirradiation.

Oxidation, as well as carbon-carbon bond formation and reduction, is an essential and important field in synthetic chemistry.<sup>1</sup> Although a variety of methods for oxidation of alcohols have been developed by many workers over many years,<sup>2</sup> these methods are sometimes problematic because many reagents or heavy metals of environmentally high-impact are required. Benzylic alcohols and allylic alcohols, in contrast to the simple alkanols, have proved to be effectively oxidized to the corresponding aldehydes or ketones with active  $MnO_2$ ,<sup>3</sup> however, the activity of  $MnO_2$  often varies according to the way of pre-treatment and a large amount of  $MnO_2$  is required. Furthermore, Swern oxidation, which is a typical oxidation method of aldehydes, while this procedure is tedious, and halogenated solvents of environmentally high-impact and a large amount of several reagents such as DMSO and oxalyl chloride, which are not suitable for a large-scale reaction, are required.<sup>2</sup> In the course of our investigation on the application of photo-reaction to synthetic chemistry, we have found that benzylic alcohols and allylic alcohols provide the corresponding benzaldehydes and  $\alpha,\beta$ -unsaturated aldehydes with iodine under photoirradiation conditions (Scheme 1).<sup>4</sup> In this letter, we report our study of this new oxidation method.



Scheme 1

Table 1 shows the results of photooxidation of cinnamyl alcohol (**1**, 50 mg) to cinnamaldehyde (**2**) in the presence of  $I_2$  in several solvents using 400-W high-pressure mercury lamps at room temperature under aerobic conditions.<sup>5</sup> Among the solvents examined, *i*-Pr<sub>2</sub>O was found to afford the best results, and gave **2** in 95% yield (entries 1, 8–13). This reaction was completed in 12 h, while the starting material was recovered in 6 h (entry 2). Although a stoichiometric amount of  $I_2$  was required to give **2** in high yield, this oxidation was, surprisingly, promoted even by a catalytic amount of  $I_2$  (entries 3 and 4). On the other hand, the result that, without either  $I_2$  or irradiation, **2** was obtained only in low yield shows the necessity of both  $I_2$  and irradiation for this reaction (entries 5 and 6). This reaction proceeded smoothly under aerobic condition; however, the yield of **2** was reduced under a flow of argon due to the formation of many by-products (entry 7).

**Table 1.** Study of reaction conditions for oxidation of cinnamyl alcohol (**1**) to cinnamaldehyde (**2**)

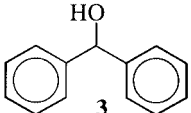
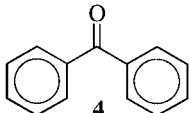
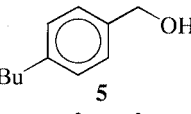
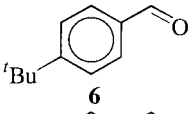
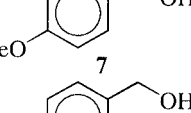
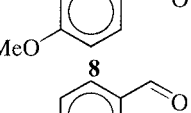
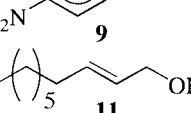
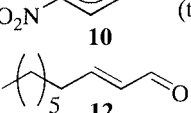
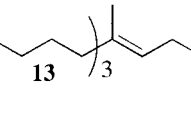
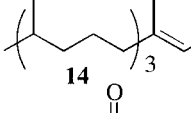
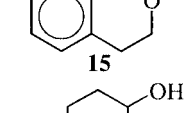
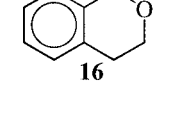
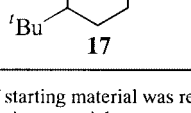
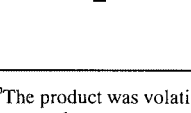
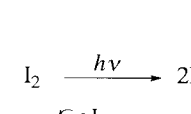
Entry	Solvent	$I_2$ / equiv	$t$ / h	Recovery of <b>1</b> / %	Yield of <b>2</b> / %
1	<i>i</i> -Pr <sub>2</sub> O	1	12	0	95
2	<i>i</i> -Pr <sub>2</sub> O	1	6	9	84
3	<i>i</i> -Pr <sub>2</sub> O	0.3	12	0	83
4	<i>i</i> -Pr <sub>2</sub> O	2	12	0	99
5	<i>i</i> -Pr <sub>2</sub> O	0	12	81	3
6	<i>i</i> -Pr <sub>2</sub> O	1	12	72	12 <sup>a</sup>
7	<i>i</i> -Pr <sub>2</sub> O	1	12	0	18 <sup>b</sup>
8	acetone	1	12	0	25
9	hexane	1	12	0	19
10	CH <sub>2</sub> Cl <sub>2</sub>	1	12	0	37
11	THF	1	12	15	75
12	toluene	1	12	0	75
13	MeCN	1	12	24	10

<sup>a</sup>The reaction was carried out in the dark. <sup>b</sup>The reaction was carried out under a flow of Ar.

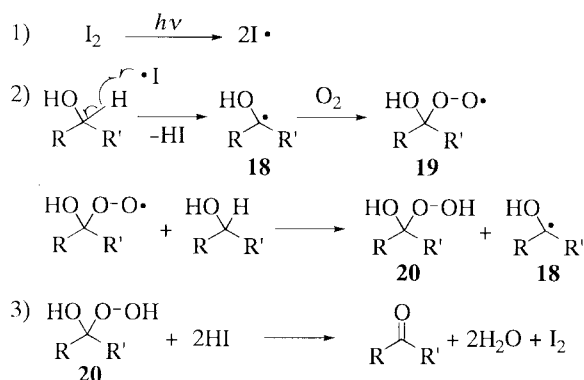
Other benzylic alcohols (**3**, **5**, **7**) and allylic alcohols (**11** and **13**) also afforded the corresponding carbonyl compounds (Table 2). Benzylic alcohols, generally, gave the products in better yield than that obtained with allylic alcohols. Benzhydrol (**3**) was oxidized to benzophenone (**4**) in high yield (97%) in the presence of 1 equiv of  $I_2$  (entry 1). 4-*tert*-Butylbenzyl alcohol (**5**) and 4-methoxybenzyl alcohol (**7**) were less reactive than **3**,<sup>6,7</sup> and 4-*tert*-butylbenzaldehyde (**6**) and 4-methoxybenzaldehyde (**8**) were obtained in 77% and 57% yield, respectively, after 48 h (entries 2 and 3). In contrast, 4-nitrobenzyl alcohol (**9**), which possess an electron-withdrawing group, resisted this oxidation conditions, and 92% of the starting material was recovered (entry 4). *trans*-2-Decenal (**12**) and phytanal (**14**) were obtained in moderate yields, when *trans*-2-decen-1-ol (**11**) and phytol (**13**), which are allylic alcohols, were used as substrates (entries 5 and 6). In addition, isochromanone (**16**), which is a benzyl ether, was directly oxidized to isochromanone (**16**) in 26% yield (entry 7). Unfortunately, 4-*tert*-butylcyclohexyl alcohol (**17**), which is a simple alkanol, was intact under the conditions, and only the starting material was recovered quantitatively even after 66 h (entry 8). Furthermore, this method is effective for gram-scale reaction: 77% of **2** was obtained when 1 g of **1** was used in a vessel under the similar conditions.<sup>8</sup>

Although the mechanism of this oxidation is not yet clear, oxygen in air plays an important role to proceed this reaction

**Table 2.** Photooxidation of benzylic alcohols and allylic alcohols with I<sub>2</sub>

Entry	Substrate	t / h	Product (yield / %)
1		24	 (97)
2		48	 (77)
3		48	 (57)
4		48	 (trace) <sup>d</sup>
5		24	 (45) <sup>b</sup>
6		12	 (54)
7		24	 (26)
8		66	— <sup>c</sup>

<sup>a</sup>92% of starting material was recovered. <sup>b</sup>The product was volatile.  
<sup>c</sup>The starting material was quantitatively recovered.

**Scheme 2**

smoothly since the yield of the carbonyl product was reduced under a flow of argon. As shown in Scheme 2, iodine radical, which is generated under the photoirradiation conditions, abstracts the hydrogen atom at benzylic position of the starting material.<sup>9</sup> The resulting radical species **18** reacts with molecular oxygen to generate the peroxy radical species **19**, which produce **20** and **18** through the autoxidation path. The hydroperoxide **20** is thought to be reduced by hydrogen iodide, which is generated in situ, to the corresponding carbonyl product.<sup>10</sup> We have no evidences for the intermediates in this path, and a more detailed study is now in progress in our laboratory.

In conclusion, this new method for the preparation of benzaldehydes and  $\alpha,\beta$ -unsaturated aldehydes is thought to be environmentally friendly, due to both the use of *i*-Pr<sub>2</sub>O of environmentally low-impact as solvent and of no heavy metals.

**References and Notes**

- 1 F. A. Carey and R. J. Sundberg, "Advanced Organic Chemistry: Reactions and Synthesis", Plenum Pub Corp., New York (1990).
- 2 "Comprehensive Organic Transformations: A Guide to Functional Group Preparations," ed. by R. C. Larock, Wiley-VCH, New York (1989).
- 3 A. J. Fatiadi, *Synthesis*, **65**, 133 (1976) and see the references cited therein.
- 4 In the presence of iodine, alcohols are oxidized by electrochemical method or metals: Z. Ogumi, S. Ohashi, Z. Takehara, *Electrochim. Acta*, **30**, 121 (1985); Y. N. Kukushkin, V. N. Demidov, N. P. Fedyanin, *Zh. Obshch. Khim.*, **53**, 2393 (1983); M. L. Mihailovic, Z. Cekovic, J. Stankovic, *J. Chem. Soc. D*, **1969**, 981.
- 5 A typical procedure is as follows: A solution (5 mL) of the cinnamyl alcohol (50 mg) and I<sub>2</sub> in *i*-Pr<sub>2</sub>O was irradiated at room temperature with a 400-W high-pressure mercury lamp externally for the indicated time. The reaction mixture was then diluted with diethyl ether and washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln and brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Pure product was obtained after purification by preparative TLC.
- 6 **5** was recovered in 8% after 24 h.
- 7 Excess amount of I<sub>2</sub> (2 equiv) was not effective: the yield of **6** was reduced and 18% of **5** was recovered after 24 h.
- 8 A procedure is as follows: A solution (50 mL) of the cinnamyl alcohol (1 g, 7.5 mmol) and I<sub>2</sub> (0.95 g, 3.7 mmol) in *i*-Pr<sub>2</sub>O was irradiated at room temperature with a 400-W high-pressure mercury lamp externally for 12h. The reaction mixture was then diluted with diethyl ether and washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln and brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Pure product was obtained after purification by SiO<sub>2</sub> column chromatography.
- 9 F. B. Mallory and C. W. Mallory, *Org. React.*, **30**, 1 (1984).
- 10 We believe that iodine is re-produced in situ, since the dark brown color of the reaction mixture seemed to remain unchanged as such.