Aerobic Oxidation of Benzyl- and Allylic Alcohols under Visible Light Irradiation of a Fluorescent Lamp in the Presence of Catalytic Iodine

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Benzyl alcohols and allylic alcohols were found to be oxidized to the corresponding aldehydes in the presence of a catalytic amount of iodine under irradiation of a fluorescent lamp.

Key words aerobic oxidation; aldehyde; allyl alcohol; benzyl alcohol; catalytic iodine

Aldehydes are important intermediates for many chemical products, and synthetic methods of these compounds have been developed from the viewpoint of both oxidation and reduction for a long time. Although a variety of methods for oxidation of alcohols to aldehydes, especially, have been extensively developed, these methods are sometimes problematic because many reagents or heavy metals of environmentally high impact are required.1) Regarding benzylic alcohols and allylic alcohols, in contrast to the simple alkanol, they have proved to be effectively oxidized to the corresponding aldehydes or ketones with active MnO2; however, there are some limitations of this new non-metal oxidation method (Chart 2). Among the solvents examined, ethyl acetate was found to exhibit the highest activity (entries 10, 11). Cinnamyl alcohol, which is a heterocyclic alcohol, afforded the corresponding benzaldehyde (entry 12).

Table 1 shows the results of a study of reaction conditions conducted with 4-tert-butylbenzylalcohol (1) as a test substrate under the conditions of 10- or 24-h external irradiation by a general-purpose fluorescent lamp in the presence of a catalytic amount of iodine in an oxygen atmosphere.17,18) Among the solvents examined, ethyl acetate was found to be the most effective solvent for 4-tert-butylbenzaldehyde (2) (entries 1—5). We were surprised to find that the yield of 2 was gradually reduced when the amount of iodine was increased (entries 5, 9—11). The reason is not clear yet; however, we believe that decrease of the transmission of light due to an increase of the dissolving iodine is cause. That no oxidation proceeded without either irradiation by a fluorescent lamp or the addition of iodine shows the necessity of both for this reaction (entries 7, 12). Furthermore, from the fact that yields of the target substance were reduced substantially when conducting the reaction under the flow of argon, we can assume that the actual oxidant in this reaction is molecular oxygen (entry 8).

Table 2 shows the scope and limitations of this oxidation reaction using a variety of alcohols. Benzyl alcohols, in general, afford the corresponding benzaldehydes in high yields regardless of an electron-donating group or electron-withdrawing group at the aromatic nucleus, and primary or secondary alcohols; however, the reactivity of 5 was found to be different from others9) (entries 1—7). Cinnamyl alcohol (15), which is an allylic alcohol, afforded cinnamaldehyde (16) in 56% yield due to generation of several unidentified by-products. On the other hand, 3-pyridinemethanol (17), which is a heterocyclic alcohol, afforded the corresponding aldehyde 18 in a trace amount and most of 17 was recovered. Furthermore, dodecanol (19), an aliphatic alcohol, was intact, and the starting material was recovered quantitatively (entry 10).

Chart 2 shows a possible path of this oxidation, which is postulated by considering the necessity of continuous irradiation,20) a catalytic amount of iodine and molecular oxygen in this reaction. The radical species 20, which is generated in Eq. 2 (Eq. 3). Aldehyde 21 was af-
In conclusion, this new method for the preparation of benzaldehydes and \(\alpha,\beta\)-unsaturated aldehydes is convenient in the viewpoint of using visible light irradiated from a general-purpose fluorescent lamp instead of UV light from a high-pressure mercury lamp, and is thought to be environmentally benign, due to all the factors of the use of molecular oxygen as terminal oxidant, EtOAc of environmentally low impact as solvent, catalytic amount of iodine and no metals. The study of scale-up of this reaction is now in progress in our laboratory.

References and Notes


14) A typical procedure follows: A dry ethyl acetate solution (5 ml) of the \(4\) -tert-butybenzylalcohol (0.3 mmol) and I\(_2\) (0.03 mmol) in a Pyrex test tube equipped with an O\(_2\)-balloon, was stirred and irradiated at room temperature for 24 h with four of 22-W fluorescent lamps, which was set from the test tube in the distance of 80 mm. The reaction mixture was concentrated under reduced pressure, and dissolved in diethyl ether, and washed with sodium thiosulfate and brine. The organic layer was dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The pure product was obtained by preparative tlc.

15) The yield of \(2\) under air was lower than that under oxygen atmosphere.

16) The yield of \(2\) under discontinuous of irradiation was much lower than that under the usual conditions.