

Aerobic oxidation under visible light irradiation of a fluorescent lamp with a combination of carbon tetrabromide and triphenyl phosphine

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Received 25 August 2007; revised 23 October 2007; accepted 26 October 2007

Available online 30 October 2007

Abstract—A combination of $\text{CBr}_4\text{-Ph}_3\text{P}$, a non-metal method, enables us to carry out aerobic photo-oxidation of alcohols and aromatic methyl groups to the corresponding carboxylic acids under irradiation of vis from a general-purpose fluorescent lamp. Aliphatic primary- and secondary alcohols, benzyl alcohols, and methyl groups at the aromatic nucleus generally afforded the carboxylic acids directly in good to high yield.

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The notion of green chemistry is becoming well established, and the development of environmentally benign processes is the goal of various research projects.¹ A method using molecular oxygen is one way consistent with this notion due to its high atom economy or E-factor as an oxidant.^{2,3} With this background in mind, we have been engaged in aerobic oxidation of alcohols and a methyl group at the aromatic nucleus under irradiation of UV with several bromo sources.⁴ We believe that the bromo radical, formed by continuous aerobic photo-oxidation of the bromo anion, effects these reactions. This is the driving force of our further studies on this oxidation with a new bromo source, which releases the bromo anion more easily under a non-metal condition, and we have found that a combination of CBr_4 and PPh_3 is suitable for oxidation of alcohols and a methyl group at the aromatic nucleus. In addition, surprisingly, this oxidation was found to proceed smoothly even under irradiation of visible light (vis) by a general-purpose fluorescent lamp instead of UV by a high-pressure mercury lamp. The effective use of vis is a most important research topic at this time of hoped-for development of new energy conversion and energy-using technology, and our new oxidation method is interesting since there

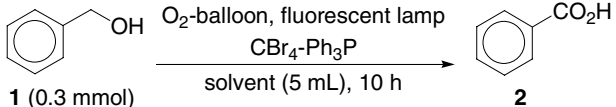
have been no reports about the application of photo-oxidation with vis by a general-purpose fluorescent lamp to fine chemistry. Although a combination of CBr_4 and PPh_3 has been widely used as brominating reagents of hydroxyl groups¹ due to its easy generation of a bromo anion, there have been no reports about the application of it to fine chemistry as an oxidizing reagent so far. Thus, we now report our detailed study for visible light aerobic oxidation of alcohols and an aromatic methyl group in the presence of a catalytic amount of $\text{CBr}_4\text{-Ph}_3\text{P}$.

Table 1 shows the results of our study of reaction conditions for the aerobic oxidation conducted with benzyl alcohol (**1**, 0.3 mmol) as test substrate in the presence of additives in typical solvents equipped with an oxygen balloon. Among the solvents and the amount of the additives examined, acetonitrile,⁵ and 0.1 equiv of CBr_4 and Ph_3P was found to be suitable for the reaction, respectively.

Table 2 shows the results for oxidation of several substrates under the reaction conditions mentioned above. Benzyl alcohols were found to give the corresponding benzoic acids in high yield regardless of an electron-donating or electron-withdrawing group at the aromatic nucleus (entries 1–8). Furthermore, 3-thiophenemethanol (**17**), which is a heterocyclic substrate, afforded 3-thiophenecarboxylic acid (**18**) in 80% yield (entry 9). Aliphatic primary alcohols generally afforded the

Keywords: Aerobic oxidation; Carbon tetrabromide; Fluorescent lamp; Triphenylphosphine; Visible light.

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Table 1. Study of reaction conditions for the photo-oxidation of benzylalcohol (**1**)^a


Entry	CBr ₄ /PPh ₃ (equiv)	Solvent	Yield of 2 ^b (%)
1	0.1/0.1	EtOAc	74
2	0.1/0.1	Hexane	0 ^c
3	0.1/0.1	Acetone	0 ^c
4	0.1/0.1	MeOH	0
5	0.1/0.1	MeCN	100
6	0.1/0.1	MeCN	0 ^d
7	0.1/0.1	MeCN	0 ^e
8	0.1/0.01	MeCN	93
9	0.1/0.05	MeCN	96
10	0.05/0.05	MeCN	98
11	0.01/0.01	MeCN	0
12	—/0.1	MeCN	0
13	0.1/—	MeCN	0

^a A solution of alcohol (0.3 mmol) additive in dry solvent (5 mL) in Pyrex test tube was irradiated with fluorescent lamp (22 W × 4) for 10 h.

^b All yields are for pure, isolated products.

^c A trace amount of benzaldehyde was detected.

^d The reaction was carried out in the dark.

^e The reaction was carried out under N₂.

corresponding carboxylic acids in good yield; however, secondary alcohols were found to give the corresponding carbonyl compounds in low yield (entries 10 and 11).⁶ Regarding oxidation of the aromatic methyl group,

in which ethyl acetate was the most suitable solvent,⁷ an electron-donating group at the aromatic nucleus accelerates the reactions, and affords the corresponding carboxylic acids in high yield; however, electron-withdrawing groups at the aromatic nucleus retarded the reactions, and yields of the products were zero to modest (entries 12–19). On the other hand, N-heterocyclic compounds, 3-pyridinemethanol and picoline, were also employed in this reaction; however, only the starting material was recovered quantitatively.⁸

To examine the mechanism of this reaction, at first, **1** was subjected to irradiation for 5 h with a fluorescent lamp and then reacted in the dark for 5 h, and lowering of the yield⁹ shows the necessity of continuous irradiation to complete this oxidation, and this reaction does not involve an auto-oxidation path. Also, this reaction includes bromine formation because the color of the reaction mixture immediately changed to yellow under irradiation of the lamp. We present in Scheme 1 what we assume is a plausible path of this oxidation, which is postulated by considering all of the results mentioned above, and the necessity of a catalytic amount of CBr₄, Ph₃P and of molecular oxygen in this reaction. Regarding the oxidation of alcohols, the radical species **33** is thought to be generated by abstraction of a hydrogen radical with a bromo radical, formed by continuous aerobic photo-oxidation of the bromo anion from CBr₄ (Eqs. 1–3). Solvation effect of ethyl acetate or acetonitrile on the phosphonium salt is thought to be suitable for liberating the ‘naked’ bromo anion, and the bromo radical is generated comparatively easily even

Table 2. Aerobic photo-oxidation with fluorescent lamp^a

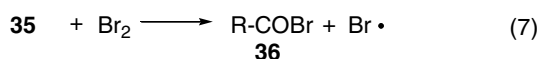
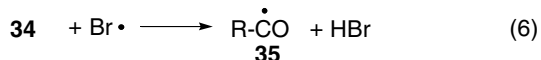
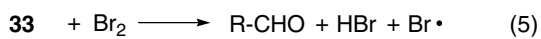
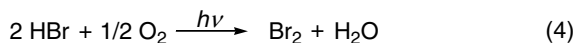
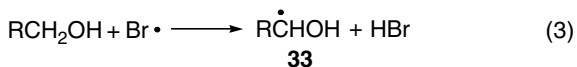
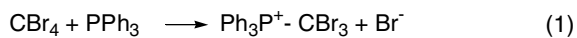
Entry	Substrate	Solvent ^b	Product	Yield ^c (%)
1	Benzylalcohol (1)	AN	Benzoic acid (2)	100
2	4- ^t Bu-benzylalcohol (3)	AN	4- ^t Bu-benzoic acid (4)	94
3	4-Chlorobenzylalcohol (5)	AN	4-Chlorobenzoic acid (6)	87
4	4-Methoxybenzylalcohol (7)	AN	4-Methoxybenzoic acid (8)	99
5	4-Nitrobenzylalcohol (9)	AN	4-Nitrobenzoic acid (10)	96
6	<i>sec</i> -Phenethylalcohol (11)	AN	Acetophenone (12)	83
7	1-Naphthalenemethanol (13)	AN	1-Naphthoic acid (14)	88
8	2-Naphthalenemethanol (15)	AN	2-Naphthoic acid (16)	70
9	3-Thiophenemethanol (17)	AN	3-Thiophenecarboxylic acid (18)	80
10	1-Dodecanol (19)	EA	1-Dodecanoic acid (20)	94
11	2-Dodecanol (21)	EA	Dodecan-2-one (22)	55 ^d
12	Toluene (23)	EA	Benzoic acid (2)	99
13	4- ^t Bu-toluene (24)	EA	4- ^t Bu-benzoic acid (4)	90
14	4-Methoxytoluene (25)	EA	4-Methoxybenzoic acid (8)	100
15	4-Phenyltoluene (26)	EA	4-Phenylbenzoic acid (27)	90
16	4-Chlorotoluene (28)	EA	4-Chlorobenzoic acid (6)	86
17	4-Cyanotoluene (29)	EA	4-Cyanobenzoic acid (30)	60
18	4-Nitrotoluene (31)	EA	4-Nitrobenzoic acid (10)	0
19	1-Methylnaphthalene (32)	EA	1-Naphthoic acid (14)	22

^a A typical procedure follows: A solution of alcohol (0.3 mmol), CBr₄ (0.1 equiv), Ph₃P (0.1 equiv) in dry ethyl acetate (5 mL) in Pyrex test tube was irradiated with fluorescent lamp (22 W × 4) for 10 h.

^b AN; acetonitrile, EA; ethyl acetate.

^c All yields are for pure, isolated products.

^d The reaction was carried out for 24 h.



Scheme 1. Plausible path of the aerobic photo-oxidation of alcohols.

under irradiation of vis. Bromine, then, was formed by aerobic photo-oxidation of hydrogen bromide, which is generated in Eq. 3 (Eq. 4). We believe that the oxidation was not observed when using 3-pyridinemethanol and picoline as substrate since they trap this hydrogen bromide at the N-atom.¹⁰ Aldehyde **34**¹¹ was afforded by abstraction of a hydrogen radical with bromine (Eq. 5), and the re-generated bromo radical abstracted a hydrogen radical from **34** to give radical species **35**, which was transformed to acyl bromide **36** (Eqs. 6 and 7).¹² The carboxylic acid was formed by reaction with water, generated in Eq. 4, although there was a possibility that the dissolved water in the solvent effected the reaction (Eq. 8).

In conclusion, we have found a facile method for aerobic oxidation of alcohols and a methyl group at the aromatic nucleus directly to the corresponding carboxylic acid in the presence of a catalytic amount of CBr_4 – Ph_3P under visible light irradiated from a general-purpose fluorescent lamp. This new form of oxidation reaction is interesting due to the non-use of metals and halogenated solvents, waste reduction, and the use of molecular oxygen.¹³

Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2007.10.132](https://doi.org/10.1016/j.tetlet.2007.10.132).

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- Among our study, acetonitrile was a suitable solvent for alcohols and ethyl acetate was suitable for a methyl group at the aromatic nucleus, respectively, see [Supplementary data](#).
- The radical species of secondary alcohols are, in general, generated easier than that of primary ones. Unfortunately, we do not have any direct data to explain this result, and the study is now in progress in our laboratory.
- Since transesterification of the substrate alcohols occurred when using ethyl acetate as solvent, we generally used acetonitrile when using alcohols as substrates and ethyl acetate when using aromatic methyl group as substrates.
- We also examined with 4-methyl benzyl alcohol to study the selectivity between alcohol and methyl group, and we could obtain 4-methylbenzoic acid in 60% yield as the main product. Alcohol is relatively easily oxidized than methyl group; however, the selectivity is not so clear.
- Only 19% of **2** was obtained.
- Although we examined this reaction with 3-methylpyrrole as test substrate, the complex mixture was obtained instead of the corresponding carboxylic acid.

11. The reaction is thought to proceed through an aldehyde as an intermediate since **2** was obtained in 88% yield when benzaldehyde was subjected to the same aerobic photo-oxidation conditions.
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13. This oxidation method is also applicable to mol scale conditions, and **4**, for example, was obtained in 77% yield when using **24** as substrate under similar conditions mentioned above.