Supplementary Material (ESI) for Green Chemistry

SUPPLEMENTARY INFORMATION

Aerobic Visible Light-Oxidation of a Methyl Group at the Aromatic Nucleus

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General Material and Equipment: Dry ethyl acetate, hexane, acetone, and acetonitrile were purchased from Kanto Chemical Co., Ltd. Dry diethyl ether was prepared with sodium. 4-*tert*-butyltoluene, 4-phenyltoluene, 4-methoxytoluene, 4-cyanotoluene, 4-nitrotoluene, 2-methylnaphthalene, 3-methylthiophene, 2-picoline were purchased from Tokyo Kasei Kogyo Co., Ltd. Sodium bromide, potassium bromide and cesium bromide were purchased from Wako Pure Chemical Industries, Ltd. Lithium bromide was purchased from Kishida Chemical Co. Ltd., and all other metal bromide were purchased from Sigma-Aldrich Co. All chemicals were used without further purification. Preparative T. L. C. plates (1.005744.00) were purchased from Merk Ltd. All experiments were carried out in a pyrex glass test tube fitted with an O_2-balloon. The ^{1}H-NMR spectrum was recorded on JEOL 400-MHz spectrometer (EX-400 and AL-400) using TMS as an internal standard or solvent peak as a standard. All of the products are known compounds.

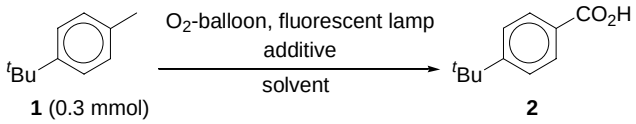
General Procedure for the Photo-oxidation with Fluorescent Lamp:

A solution of substrate (0.3 mmol), magnesium bromide diethyl etherate (15.5 mg, 0.2 equiv.) in dry ethyl acetate (2.5 mL) in a pyrex glass test tube fitted with an O_2-balloon was irradiated by general-purpose fluorescent lamp (22W x 4) for 10 hr. The reaction mixture was concentrated under reduced pressure, and the residue was diluted with diethyl ether and extracted three times with 10% aq. NaOH. The aqueous layer was collected and acidified with 6% aq. HCl, and then extracted three times with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$, and filtered. The ether layer was concentrated under reduced pressure and dried under vacuum. The obtained product did not require further purification.

Optimization of Photo-Oxidation with Fluorescent Lamp :

Table 1 shows the results for study of reaction conditions using 4-*tert*-butyltoluene (**1**, 0.3 mmol) as the test substrate. A variety of metal bromides (0.2 equiv.) in various solvents were used. Reactions were performed for 7 to 24 hours in a pyrex glass test tube fitted with an O_2-balloon. Among the solvents and the metal bromides examined, ethyl acetate and magnesium bromide diethyl etherate were found to be most suitable for the reaction.

Table 2. Study of Reaction Conditions for the Photo-oxidation of 4-*tert*-Butyltoluene (**1**)



1 (0.3 mmol) **2**

entry	additive	(eq.)	solvent	(ml)	time (h)	yield of **2** (%)[a]
1	$MgBr_2Et_2O$	(0.2)	hexane	(5)	10	23
2	$MgBr_2Et_2O$	(0.2)	acetone	(5)	10	0
3	$MgBr_2Et_2O$	(0.2)	MeCN	(5)	10	0
4	$MgBr_2Et_2O$	(0.2)	Et_2O	(5)	10	0
5	$MgBr_2Et_2O$	(0.2)	H_2O	(5)	10	0
6	$MgBr_2Et_2O$	(0.2)	EtOAc	(5)	10	87
7	$MgBr_2Et_2O$	(0.2)	EtOAc	(5)	7	79
8	$MgBr_2Et_2O$	(0.2)	EtOAc	(5)	24	71
9	$MgBr_2Et_2O$	(0.1)	EtOAc	(5)	10	72
10	$MgBr_2Et_2O$	(0.3)	EtOAc	(5)	10	79
11	$MgBr_2Et_2O$	(0.4)	EtOAc	(5)	10	71
12	$MgBr_2Et_2O$	(1.0)	EtOAc	(5)	10	0
13	$MgBr_2Et_2O$	(0.2)	EtOAc	(2.5)	10	86
14	$MgBr_2Et_2O$	(0.1)	EtOAc	(2.5)	10	86[b]
15	$MgBr_2Et_2O$	(0.2)	EtOAc	(2.5)	10	98[b]
16	$MgBr_2Et_2O$	(0.3)	EtOAc	(2.5)	10	94[b]
17	$MgBr_2Et_2O$	(0.2)	EtOAc	(7.5)	10	84
14	LiBr	(0.2)	EtOAc	(2.5)	10	0
15	NaBr	(0.2)	EtOAc	(2.5)	10	0
16	KBr	(0.2)	EtOAc	(5)	10	0
17	CsBr	(0.2)	EtOAc	(2.5)	10	0
18	$CaBr_2$	(0.2)	EtOAc	(2.5)	10	82
19	$SrBr_2$	(0.2)	EtOAc	(2.5)	10	0
20	$BaBr_2$	(0.2)	EtOAc	(2.5)	10	0
21	$TiBr_4$	(0.2)	EtOAc	(2.5)	10	61
22	$ZrBr_4$	(0.2)	EtOAc	(2.5)	10	72
23	$NbBr_5$	(0.2)	EtOAc	(2.5)	10	59
24	$MoBr_3$	(0.2)	EtOAc	(2.5)	10	61
25	$CoBr_2$	(0.2)	EtOAc	(2.5)	10	0
26	$NiBr_2$	(0.2)	EtOAc	(2.5)	10	0
27	CuBr	(0.2)	EtOAc	(2.5)	10	0
28	$CuBr_2$	(0.2)	EtOAc	(2.5)	10	0
29	AgBr	(0.2)	EtOAc	(2.5)	10	0
30	$ZnBr_2$	(0.2)	EtOAc	(2.5)	10	0
31	$AlBr_3$	(0.2)	EtOAc	(2.5)	10	88
32	$GaBr_3$	(0.2)	EtOAc	(2.5)	10	0
33	$SbBr_3$	(0.2)	EtOAc	(2.5)	10	68
34	$LaBr_3$	(0.2)	EtOAc	(2.5)	10	91
35	$SmBr_3$	(0.2)	EtOAc	(2.5)	10	99
36	$EuBr_2$	(0.2)	EtOAc	(2.5)	10	92
37	$YbBr_3$	(0.2)	EtOAc	(2.5)	10	78

[a] The yields are for pure, isolated products.
[b] The reaction was carried out without stirring.

Spectral Distribution of Fluorescent lamp used for the Reaction:

Fig. 1 shows the results for analysis of spectral distribution of the fluorescent lamp used for this reaction. The spectrum was recorded on HSU-100S (Asahi Spectra Co., Ltd.).

Fig. 1 Spectral Distribution of Fluorescent lamp used for the Reaction