SUPPORTING INFORMATION

Facile Solar Oxidation of Alcohols with Molecular Oxygen

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Experimental Section

General Equipment and Material: All experiments were carried out in a pyrex glass test tube with a ground-glass joint. The ^{1}H-NMR spectrum was recorded on a JEOL EX-400 and JEOL AL-400 instrument using $CDCl_3$, CD_3OD or d_6-DMSO as the solvent with TMS as an internal reference. 1-Dodecanol, 4-*tert*-butylbenzyl alcohol, 4-chlorobenzyl alcohol, 2-dodecanol, 4-*tert*-butylcyclohexanol, 1-phenylethyl alcohol, 2-phenylethyl alcohol, were purchased from Tokyo Kasei Kogyo Co., Ltd. Sodium bromide, sodium iodide, potassium bromide and cesium bromide were purchased from Wako Pure Chemical Industries, Ltd. Lithium bromide was purchased from Kishida Chemical Co. Ltd. All chemicals were used without further purification. Dry ethyl acetate, hexane, acetone, acetonitrile, *i*-propylether and benzene were purchased from Kanto Chemical Co., Ltd. Dry THF was prepared with sodium. Amberlyst 15 was purchased from Organo Co. and Dowex 50Wx8 was purchased from Muromachi Chemical Inc. NaY was purchased from TOSOH Co. H-ZSM-5 was obtained from NE CHEM CAT Co. TiO_2 was purchased from Wako Pure Chemical Industries, Ltd. Silica gel (230-400 mesh) was purchased from Merk Ltd. FSM-16 and 10% Ti-HMS were prepared as described previously (see references 7 and 10, respectively). Preparative T. L. C. plates (1.005744.00) were purchased from Merk Ltd.

General Procedure for the Solar Oxidation with Molecular Oxygen:

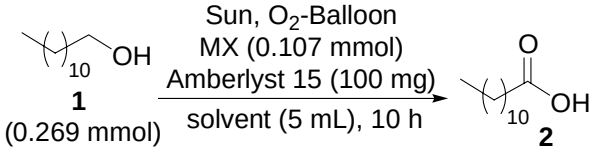
Primary Alcohols: A suspension of alcohol (0.269 mmol), sodium bromide (5.5 mg, 0.054 mmol) and Amberlyst 15 (25 mg) in dry ethyl acetate (5 mL) in a pyrex glass test tube was irradiated in the sun for 10 hr (from 7 Am to 5 PM on a clear day). Solid reagents were filtered off and washed with ethyl acetate and the filtrate was then concentrated under reduced pressure. The residue was diluted with 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 ether. The ether layer was dried over anhydrous $MgSO_4$, and filtered. The ether layer was concentrated under reduced pressure and dried in a desiccator under vacuum. The obtained product did not require further purification.

Secondary Alcohols: A suspension of alcohol (0.269 mmol), sodium bromide (5.5 mg, 0.054 mmol) and Amberlyst 15 (25 mg) in dry ethyl acetate (5 mL) in a pyrex glass test tube was irradiated with sunlight for 10 hr (from 7 Am to 5 PM on a clear day). Solid reagents were filtered off and washed with ethyl acetate. The filtrate was then concentrated under reduced pressure. A pure product was obtained by preparative T.L.C. with a mixed solvent of hexane and ethyl acetate as developing solvent.

Optimization of Solar Oxidation:

Table 1: Initial studies of the reaction conditions were carried out using 1-dodecanol (**1**, 50 mg, 0.269 mmol) as the test substrate. A combination of Amberlyst 15 (100 mg) and several alkali metal halides (0.107 mmol) in various solvents were used. Reactions were performed for 10 hours (from 7 AM to 5 PM on a clear day) in a pyrex glass test tube fitted with an oxygen balloon. Among the solvents and the alkali metal halides examined, ethyl acetate and sodium bromide were found to be most suitable for the reaction.

Table 1. Study of Reaction Conditions for Solar Oxidation



entry	solvent	MX	yield (%) [a, b]	
1	Hexane	NaBr	0	
2	Acetone	NaBr	0	
3	MeCN	NaBr	0	
4	*i*Pr_2O	NaBr	0	
5	THF	NaBr	trace	
6	benzene	NaBr	0	
7	H_2O	NaBr	0	
8	AcOEt	NaBr	74	60
9	AcOEt	NaCl		0
10	AcOEt	NaI		0
11	AcOEt	LiBr		49
12	AcOEt	KBr		51
13	AcOEt	CsBr		47

[a] Isolated yield.
[b] Two series of reactions (entries 1-8 and 8-13) were carried out on separate days.

Figure 1. Further study of reaction conditions revealed the relationship between the amount of sodium bromide and Amberlyst 15, in which the combination of 0.2 equiv. (0.054 mmol) of sodium bromide and 25 mg of Amberlyst 15 afforded the best result for oxidation of 50 mg (0.269 mmol) of **1**.

Figure 1. Study of the Relationship between the Amount of Sodium Bromide and Amberlyst 15