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Oxidative Photodecarboxylation of α-Hydroxycarboxylic Acid Derivatives with FSM-16 under Visible Light Irradiation of Fluorescent Lamp

Norihiro TADA, Yoko MATSUSAKI, Tsuyoshi MIURA, and Akichika ITOH*

Gifu Pharmaceutical University; 1–25–4 Daigaku-nishi, Gifu 501–1196, Japan.

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Hydroxycarboxylic acids were converted to the corresponding carbonyl compounds under aerobic photo-oxidative conditions in the presence of FSM-16 under visible light irradiation by a fluorescent lamp. This synthetic protocol is the first example of FSM-16 functioning as a photocatalyst by visible light.

Key words oxidative; photodecarboxylation; α-hydroxycarboxylic acid; FSM-16; visible light

The importance of environmentally friendly processes has been recognized in all fields of industry as well as in the field of synthetic organic chemistry.[1)] Photoreactions are a promising synthetic process in this context.[2)] In particular, the development of photocatalysts is a subject that is now receiving significant attention. TiO_2, which catalyses the oxidation of NO_x and the reduction of CO_2,[3,4)] is one example of a practical and useful photocatalyst; extensive efforts have been made to develop photocatalysts that are effectively activated by visible light (VIS).[5)] Currently, the effective use of VIS is one of the most important research topics for the prospective development of new energy conversion and energy-using technology. The photoreactivity of microporous silicas[6)] containing transition metals has also been studied by many groups[7)]; however, little is known about silica itself.[8—11)] A similar trend is observed for mesoporous silicas[6)] for which there have been a few reports on the photoreactivity of silica itself.[12—18)] During our investigation in the application of mesoporous silicas to synthetic chemistry, we found that benzylic acid (**1**) is oxidatively decarboxylated by photoirradiation to give benzophenone (**2**) using a 400-W high-pressure mercury lamp in the presence of FSM-16,[16)] which is a mesoporous silica developed by Inagaki *et al.*[19,20)] In general, thermal[21—28)] and photolytic[29,30)] oxidative decarboxylation reactions of phenylacetic acid derivatives, which have been reported by several groups to proceed by using heavy metals as promoters, produce a large amount of waste and thus cause environmental problems; however, typical mesoporous silicas are free of heavy metals, recyclable, and yield little waste. Although this reaction has the advantages of both inexpensive acquisition of safe reagents and easy work-up, a 400-W high-pressure mercury lamp, which is expensive and has harmful effects on the human body, is required. This is the driving force of our continued studies under VIS light irradiation using a general-purpose fluorescent lamp. It is known that UV light is required for the photometathesis with FSM-16[14)]; to the best of our knowledge, there is no precedent for visible light photoreaction with FSM-16. Herein, we report the aerobic photodecarboxylation of α-hydroxycarboxylic acid derivatives with FSM-16 under visible light irradiation of a fluorescent lamp (Chart 1).

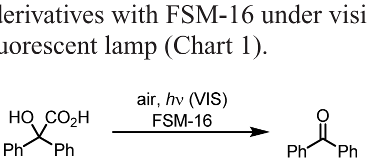
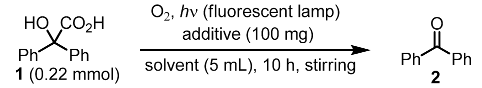


Chart 1

Results and Discussion

Table 1 shows the results of the photoreaction of benzylic acid (**1**) in the presence of additives (100 mg) in several solvents using four 22-W fluorescent lamps at room temperature. In the absence of additives, only a trace amount of benzophenone (**2**) was obtained (entry 1). Although the reaction conditions with various additives including hexagonal meso-

Table 1. Study of Reaction Conditions for Oxidative Photodecarboxylation with FSM-16



Entry	Solvent	Additive	Yield (%)[a)]	
			2	**1**
1	Hexane	None	1	29
2	Hexane	p-TsOH · H_2O	0	79
3	Hexane	Na_2CO_3	2	16
4	Hexane	SiO_2	11	53
5	Hexane	Al_2O_3	1	59
6	Hexane	HMS	3	67
7	Hexane	MCM-41	5	43
8	Hexane	H-Y	3	55
9	Hexane	Na-Y	8	62
10	Hexane	FSM-8	2	55
11	Hexane	FSM-12	61	20
12	Hexane	FSM-16	66	34
13	Cyclohexane	FSM-16	59	21
14	H_2O	FSM-16	58	42
15	Toluene	FSM-16	50	40
16	MeOH	FSM-16	33	52
17	AcOEt	FSM-16	24	29
18	None	FSM-16	18	59
19	Acetone	FSM-16	17	83
20	CH_2Cl_2	FSM-16	13	79
21	MeCN	FSM-16	13	58
22	i-Pr_2O	FSM-16	11	59
23	THF	FSM-16	5	82
24[b)]	Hexane	FSM-16	50	29
25[c)]	Hexane	FSM-16	50	18
26[d)]	Hexane	FSM-16	81	7
27[d,e)]	Hexane	FSM-16	88	2
28[f)]	Hexane	FSM-16	0	97
29[g)]	Hexane	FSM-16	0	31
30[h)]	Hexane	FSM-16	7	66

a) ^{1}H-NMR yields. *b)* FSM-16 (80 mg). *c)* FSM-16 (120 mg). *d)* 30 h. *e)* The reaction was carried out under an air atmosphere. *f)* The reaction was carried out in the dark. *g)* The reaction was carried out under reflux without $h\nu$. *h)* The reaction was carried out under Ar.

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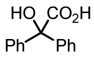
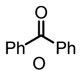
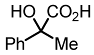
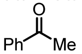
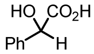
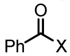
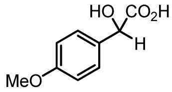
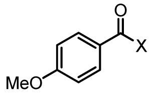
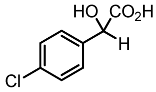
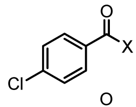
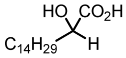
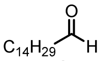
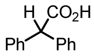
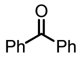
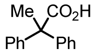
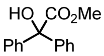
* To whom correspondence should be addressed. e-mail: itoha@gifu-pu.ac.jp

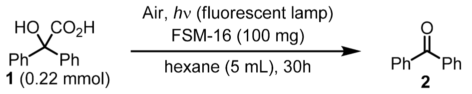
Table 2. Oxidative Photodecarboxylation of Several Substrates with FSM-16

$$\underset{(0.22\ \text{mmol})}{\text{substrate}} \xrightarrow[\text{hexane (5 mL), 30h}]{\text{Air, } h\nu \text{ (fluorescent lamp)} \atop \text{FSM-16 (100 mg)}} \text{product}$$

Entry	Substrate	Products	Yield (%)[a]
1	 **1**	 **2**	84
2	 **3**	 **4**	50
3	 **5**	 **6**: X=H **7**: X=OH	(17) 37
4	 **8**	 **9**: X=H **10**: X=OH	50 (6)
5	 **11**	 **12**: X=H **13**: X=OH	31 9
6	 **14**	 **15**	(3)
7	 **16**	 **2**	(11)
8	 **17**	No reaction	
9	 **18**	No reaction	

a) Isolated yields. Numbers in parentheses are ^{1}H-NMR yields.

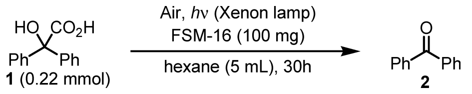
Table 3. Recycling and Reuse of FSM-16



Entry	FSM-16	Yield (%)[a]	
		2	**1**
1	Initial[b]	88	2
2	First reuse[b]	89	11
3	Second reuse[b]	66	29
4	Third reuse[b]	25	84
5	Fourth reuse[b]	20	80
6	Fifth reuse[c]	64	36

a) ^{1}H-NMR yields. *b*) Recovered FSM-16 was dried at rt for 2 h under reduced pressure and used in next reaction. *c*) Recovered FSM-16 after fourth reuse (entry 5) was recalcinated at 450 °C for 4 h and used in fifth reuse (entry 6).

Table 4. Study of Efficient Wavelength of Light



Entry	$h\nu$ (nm)[b]	Yield (%)[a]	
		2	**1**
1	Xe lamp (all)	73	27
2	397	38	43
3	445	57	53
4	499	4	55
5	558	1	99
6	589	Trace	43
7	618	0	55

a) ^{1}H-NMR yields. *b*) 300 W Xenon lamp (ASAHI SPECTRA MAX-301) was used, and light with selected wavelength was irradiated through band-pass filter.

porous silica (HMS) and MCM-41, which are mesoporous silicas, and H-Y and Na-Y, which are microporous zeolites, were varied to accomplish oxidative decarboxylation, the yields of **2** were unsatisfactory except when using FSM-12 and FSM-16[31] (entries 2—12). Moreover, when using FSM-8, a large amount of **1** was recovered, which indicates that reaction field is actually inside the pores of FSMs, because the composition and the chemical properties of FSMs are basically the same. Among the solvents examined, hexane was found to afford the best results (entry 12); however, it was found that the yield of **2** cannot be correlated to the order of solubility of oxygen (entries 12—23).[32] Benzophenone (**2**) was obtained in 81% yield by prolonging the reaction time to 30 h (entry 26). It is noted that the reaction using four 22-W fluorescent lamps requires longer reaction time (30 h) than the reaction using 400-W high-pressure mercury lamp (5 h).[16] Interestingly, the yield of **2** obtained in atmospheric air was nearly equal to that under an oxygen atmosphere (entry 27). VIS irradiation and molecular oxygen were necessary for oxidative photodecarboxylation because **2** was either not obtained or was obtained only in low yield in their absence (entries 28—30).

The results of the oxidative decarboxylation of various α-hydroxycarboxylic acids under the optimized reaction conditions are summarized in Table 2. Acetophenone (**4**) was obtained in 50% yield as the sole product when atrolactic acid (**3**) was used as a substrate (entry 2). Although mandelic acids (**5**, **8**, **11**), which are secondary α-hydroxycarboxylic acids, gave a mixture of the corresponding aldehydes and carboxylic acids in moderate yields (entries 3—5), 2-hydroxypalmitic acid (**14**)—an aliphatic acid—was converted to the corresponding aldehyde **15** only in 3% yield. Notably, diphenylacetic acid (**16**) and 2,2-diphenylpropionic acid (**17**), which possess no hydroxyl groups at the α-position, were poor substrates (entries 7 and 8), and benzilic acid methyl ester (**18**) was also intact under similar conditions, and only the starting material was recovered quantitatively (entry 9).

Next, the reuse of FSM-16 was examined (Table 3). The recovered FSM-16, which was dried at room temperature for 2 h under reduced pressure after the photoreaction with **1**, showed high activity in the reaction on first reuse to give **2** in 89% yield (entry 2). However, the yield of **2** decreased on second reuse. It was noted that the reactivity of FSM-16 was restored to a certain extent by recalcination at 450 °C for 4 h, and **2** was obtained in 64% yield.

Table 4 shows the results of the wavelengths effective for oxidative decarboxylation. The present experiments showed that visible light, especially at 445 nm, was the most effective wavelength for this reaction, and the results indicate that FSM-16 acts as a photocatalyst under visible light.

Although the mechanism of this reaction is not clear yet, the active sites, non-bonding oxygen hole center (NBOHC) and E′ center, produced by dehydration from silanol groups on the wall of FSM-16 during calcination are thought to play an important role in decarboxylation.[15]

Conclusion

We have demonstrated the oxidative photodecarboxylation of α-hydroxycarboxylic acid derivatives with FSM-16 under visible light irradiation by a fluorescent lamp. This method is significant from the viewpoint of synthetic organic chemistry because harmless visible light irradiation from a general-purpose fluorescent lamp and molecular oxygen as a terminal oxidant can be used. Further application of this photooxidation to other reactions is now in progress in our laboratory.

Experimental

General All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade, obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd. All products are known compounds and were identified by comparing their NMR spectra with those of authentic samples.

Typical Procedure (Table 2, Entry 1) A suspension of benzylic acid (**1**, 50 mg) and FSM-16 (100 mg) in dry hexane (5 ml) was irradiated with four 22-W fluorescent lamps at room temperature in atmospheric air for 30 h. FSM-16 was then filtered off and washed with ethyl acetate, and the filtrate was concentrated under reduced pressure. Pure benzophenone (**2**) (33.6 mg, 84%) was obtained after purification by preparative TLC.

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31) FSM-16 used in this study was synthesized according to ref. 8. The unit cell dimensions of this FSM-16 was 4.63 nm. The pore diameter was 2.9 nm, and the specific surface area was 882 m^2/g.
32) The solubility of O_2 in typical organic solvents, see: Che Y., Tokuda K., Ohsaka T., *Bull. Chem. Soc. Jpn.*, **71**, 651—656 (1998).