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Oxidative Photodecarboxylation of α-Hydroxycarboxylic Acids and Phenylacetic Acid Derivatives with FSM-16

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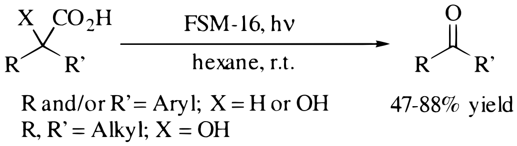
ABSTRACT



FSM-16, a mesoporous silica, was found to catalyze oxidative photodecarboxylation of α-hydroxy carboxylic acid and phenyl acetic acid derivatives to afford the corresponding carbonyl compounds. Furthermore, FSM-16 proved to be reuseable by recalcination at 450 °C after the reaction.

Recently, the importance of environmentally friendly processes has been recognized over all fields of industry and, needless to say, in the field of synthetic organic chemistry as well. Photoreaction is a promising process in this context.[1] Especially, the development of photocatalysts is a subject that is now receiving much attention. TiO_2, which catalyzes oxidation of NO_x and reduction of CO_2,[2] is one example of a practical and useful photocatalyst. The photoreactivity of microporous silicas,[3] which contain transition metals, also has been studied by many groups;[4] however, little is known about the silica itself.[5] A similar trend appears for mesoporous silicas,[3] where there is only one report on the photoreactivity of the silica itself,[6] and there are no reports regarding the application of mesoporous silicas to synthetic organic chemistry, so far. In the course of our investigation on the application of mesoporous silicas to synthetic chemistry, we have found that benzylic acid (**1**) was oxidatively decarboxylated under irradiation to give benzophenone (**2**) in the presence of FSM-16, which is a mesoporous silica developed by Inagaki,[7] and possesses high

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(1) *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S. Ed.; CRC Press: Boca Raton, 1995.

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(3) IUPAC recommends a classification of pore to micropore ($D < 2$ nm; D, pore diameter) and mesopore (2 nm $< D <$ 50 nm), see: IUPAC Manual of Symbols and Terminology, appendix 2, Part 1, Colloid and Surface Chemistry. *Pure Appl. Chem.* **1972**, *31*, 578.

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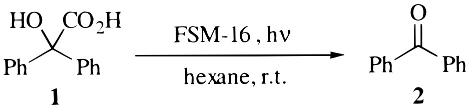
surface area, narrow pore size distribution, high pore volume, and acidic property[8] such as that of MCM-41[9] and HMS,[10] which are typical mesoporous silicas (Scheme 1).

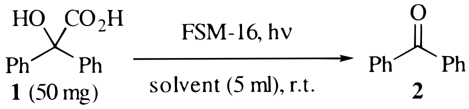
Scheme 1



Thermal[11] and photolytic[12] oxidative decarboxylation reactions of phenyl acetic 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 causes environmental problems. If FSM-16, which is free of heavy metals, is recyclable, the reaction using FSM-16 is considered to be a reaction of low environmental impact. In this letter, we report the catalytic ability of FSM-16 in the oxidative photodecarboxylation reaction of α-hydroxy carboxylic acids and phenyl acetic acid derivatives.

Table 1 shows the results of photoreaction of benzylic acid (50 mg) in the presence of FSM-16[13] (100 mg) in several solvents using 100- and 400-W high-pressure mercury lamps at room temperature.[14] Among the solvents examined, hexane was found to afford the best results (entries 1−7).[15] Without irradiation, benzophenone (**2**) was scarcely obtained even in the presence of FSM-16; on the other hand, the reaction proceeded smoothly under irradiation even with a 100-W lamp (entries 11 and 12).

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

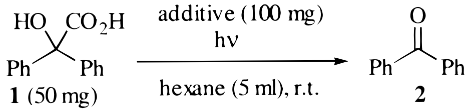


entry	solvent	*hν* (W)	FSM-16 (mg)	*t* (h)	recovery of **1** (%)	yield of **2** (%)
1		400	100	5	47	34
2	acetone	400	100	5	35	49
3	MeCN	400	100	5	32	50
4	MeOH	400	100	5	18	36[a]
5	H_2O	400	100	5	56	12[b]
6	toluene	400	100	5	21	65
7	hexane	400	100	5	<1	88
8	hexane	400	100	4	11	80
9	hexane	400	100	3	19	63
10	hexane	400	50	5	18	75
11	hexane	100	100	5	10	79
12	hexane		100	5	73	<1

[a] A total of 17% of 1,1-diphenylethylene glycol was obtained. [b] A total of 11% of benzopinacol was obtained.

Next, the effect of additives on this reaction was studied (Table 2).[16] Without additives, only a trace of the product **2** was obtained even after a longer reaction time (24 h), and 78% of the starting benzylic acid (**1**) was recovered (entry 1). MCM-41 and HMS, which are other mesoporous silicas, and H-Y, Na-Y, and H-ZSM-5, which are typical microporous zeolites, showed photoreactivity to some extent, however, they were not as effective as FSM-16 (entries 2−7). Silica gel and alumina, which are amorphous porous materials, afforded **2** in only low yields (entries 8 and 9).

Table 2. Study for Oxidative Photodecarboxylation with Several Additives



entry	additives	*t* (h)	recovery of **1** (%)	yield of **2** (%)
1		24	78	9
2	FSM-16	5	<1	88
3	MCM-41	5	25	55
4	HMS	5	44	35
5	H-Y	5	66	20
6	Na-Y	5	56	20
7	H-ZSM-5	5	30	66
8	SiO_2	5	54	23
9	Al_2O_3	5	67	10

Other α-hydroxycarboxylic acids (**3**, **5**, and **8**) also afforded the corresponding products in the same manner as **1** (Table 3). Acetophenone (**4**) was obtained in 78% yield as the sole product when atrolactic acid (**3**) was used as a substrate (entry 1). 4-Methoxymandelic acid (**5**) and 2-hydroxypalmitic acid (**8**), which are secondary α-hydroxy carboxylic acids, gave a mixture of the corresponding aldehyde and carboxylic acid (entries 2 and 3). Surprisingly,

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(11) Kim, Y. I.; Kim, Y. H. *Tetrahedron Lett*. **1998**, *39*, 639. Mohri, K.; Mamiya, J.; Kasahara, Y.; Isobe, K.; Tsuda, Y. *Chem. Pharm. Bull.* **1996**, *44*, 2218. Komuro, M.; Nagatsu, Y.; Higuchi, T.; Hirobe, M. *Tetrahedron Lett*. **1992**, *33*, 4949. Banerjee, A.; Hazra, B.; Bhattacharya, A.; Banerjee, S.; Banerjee, G. C.; Sengupta, S. *Synthesis* **1989**, 765. Fristad, W. E.; Klang, J. A. *Tetrahedron Lett*. **1983**, *24*, 2219. Giordano, C.; Belli, A.; Citterio, A.; Minisci, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1574. Santaniello, E.; Ponti, F.; Manzocchi, A. *Tetrahedron Lett*. **1980**, *21*, 2655. Dessau, R. M.; Heiba, E. I. *J. Org. Chem.* **1975**, *25*, 3647.

(12) Habibi, M. H.; Farhadi, S. *Tetrahedron Lett*. **1999**, *40*, 2821. Maki, Y.; Sako, M.; Oyabu, I.; Murase, T.; Kitade, Y.; Hirota, K. *J. Chem. Soc., Chem. Commun*. **1989**, 1780.

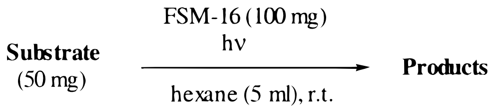
(13) FSM-16 used in this study was synthesized according to ref 7. The unit cell dimensions of this FSM-16 was 4.63 nm. The pore diameter was 2.9 nm, and the specific surface area was 882 m^2/g.

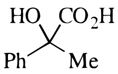
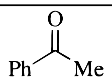
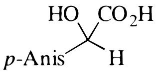
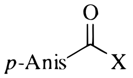
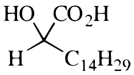
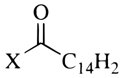
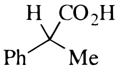
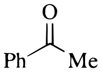
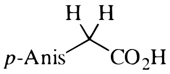
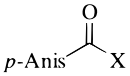
(14) A typical procedure follows: Irradiation of a suspension of benzilic acid (**1**, 50 mg) and FSM-16 (100 mg) in dry hexane (5 mL) at room temperature with a 400-W high-pressure mercury lamp for 5 h. FSM-16 was then filtered off and washed with ethyl acetate, and the filtrate was concentrated under reduced pressure. Pure benzophenone (**2**) (35 mg, 88%) was obtained after purification by preparative TLC.

(15) The solubility of O_2 in hexane is higher than that of other typical organic solvents, see: Che, Y.; Tokuda, K.; Ohsaka, T. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 651.

(16) The conversions using the additives except FSM-16 were not optimized.

Table 3. Oxidative Photodecarboxylation of Several Substrates with FSM-16

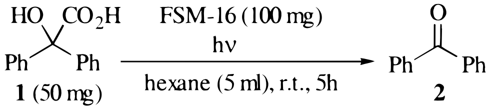


entry	substrate	t (h)	products (% yield)
1	 **3**	12	 **4** (78)
2	 **5**	12	 **6** : X=H (63) **7** : X=OH (20)
3	 **8**	15	 **9** : X=H (37) **10** : X=OH (30)
4	 **11**	60	 **4** (47)
5	 **12**	36	 **6** : X=H (30) **7** : X=OH (44)
6	n-$C_{15}H_{31}CO_2H$ **13**	48	no reaction

2-phenylpropionic acid (**11**) and 4-methoxyphenylacetic acid (**12**), which possess no hydroxyl group at the α-position, also afforded acetophenone (**4**, 47%), and a mixture of the corresponding degraded aldehyde (**6**, 30%) and carboxylic acid (**7**, 44%), respectively (entries 4 and 5). On the other hand, palmitic acid (**13**), which is a simple carboxylic acid, was unfortunately intact under the conditions, and only the starting material was recovered quantitatively even after 48 h (entry 6).

The promoter FSM-16 was found to be recyclable and useful as a photocatalyst. Thus, the recovered FSM-16, which was recalcinated at 450 °C for 4 h after the photoreaction of **1**, showed high activity in the reaction, providing 81% yield of **2** even after being reused 5 times (Table 4).

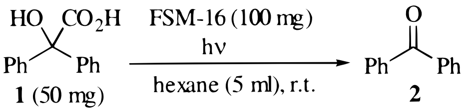
Table 4. Recycle of FSM-16



	cycle of FSM-16				
	1st	2nd	3rd	4th	5th
yield (%) of **2**	87	91	86	86	81

The mechanism of this reaction is not clear yet, however, the active sites produced by dehydration from silanol groups on the wall of FSM-16 during calcination are thought to participate in decarboxylation of the substrate.[5] An atmospheric oxygen is also concerned in this reaction as an oxidizing reagent. Table 5 shows the results of a study of the effect of oxygen. Only a small amount of product **2** was obtained under N_2, while under O_2 the yield of **2** was comparable to that under air. Since no acceleration of this reaction was observed under O_2, a high concentration of oxygen was not required; however, oxygen proved to be an important factor for this reaction. Furthermore, an attempt was made to detect the intermediates and to clarify the reaction pathway by terminating the reaction with **12** at 12 h; however, the possible intermediates, **5** or 4-methoxybenzyl alcohol (**14**), were not detected by 400 MHz NMR analysis.[17] On the other hand **14** was allowed to react under the same conditions as for **12** and found to afford **6** (9%) and **7** (3%), which were similar to results for **12**. This suggests the final oxidized products were provided by oxidation of a benzyl alcohol species as the possible intermediates. Studies on a more detailed mechanism and applications to other substrates are now in progress in our laboratory.

Table 5. Effect of Oxygen



	yield of **2** (%)		
t (h)	under N_2	under O_2	under air
3	5	61	69
5	7	73	88

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(17) The detected products of this reaction were **6** (8%) and **7** (2%). The yield was estimated on the ratio of integral value of 400 MHz NMR analysis.