Oxidative Cleavage of the Double Bonds of Styrenes with a Combination of Mesoporous Silica FSM-16 and I_2 under Photoirradiation

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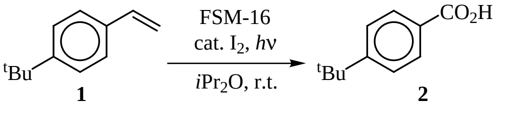
Received 29 December 2001

Abstract: A mesoporous silica FSM-16 was found to be a recyclable promoter for the oxidative cleavage of double bonds, which are conjugated with an aromatic nucleus, to afford the corresponding carboxylic acid in the presence of catalytic iodine under photoirradiation conditions.

Key words: oxidative cleavage, mesoporous silica, FSM-16, iodine, photochemistry

In general, a carbon-carbon double bond is a key functional group for transformation in organic synthesis due to its high reactivity and diversity of transformable property, and a variety of methods for transformation starting from double bonds have been developed.[1] In this context, oxidative cleavage of the double bond including ozonolysis and oxidation with a heavy metal such as ruthenium or $NaIO_4$ to afford the corresponding carboxylic acid or aldehydes is an important method.[1] Although these methods have been used for organic synthesis by many workers, it is difficult to distinguish between the double bonds except in special cases due to the high reactivity of the oxidants.[2] We have investigated the photooxidation with silicas, and a mesoporous silica FSM-16[3] was found to promote oxidation reactions at the benzylic position.[4] In the course of our study regarding the substrates and the conditions for this oxidation, FSM-16 was found to oxidize 4-*tert*-butylstyrene (**1**) to give 4-*tert*-butylbenzoic acid (**2**) exclusively in the presence of catalytic iodine under photoirradiation conditions (Scheme 1).



Scheme 1

Since FSM-16 proved to promote oxidation reactions at the benzylic position selectively in our previous studies, selective cleavage of double bonds, namely, the distinction between the double bonds which are conjugated with an aromatic nucleus and nonconjugated bonds, was expected. Now, we report our study on the generality of this oxidative cleavage with FSM-16.

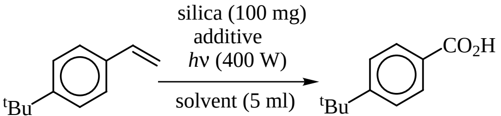
Table 1 shows the results of the transformation of 4-*tert*-butylstyrene (**1**, 50 mg) in the presence of silica (100 mg) and additives in several solvents using 400-W high-pressure mercury lamps under aerobic atmosphere at room temperature for 36 h.[5,6] Among the solvents examined, *i*-Pr_2O was found to be suitable for the reaction to afford **2** in 82% yield with FSM-16 (entries 1–10).[7] The yield of **2** was slightly increased (87%) when the reaction time was extended up to 48 h (entry 11). On the other hand, the result that, without either irradiation, oxygen, FSM-16 or iodine, **2** was not obtained or was obtained only in low yield shows the necessity of all of the foregoing conditions for this reaction (entries 12–15). Although 0.3 equiv of iodine was required to give **2** in high yield, an excess amount of iodine inhibited this oxidation (entries 16–18). Among the additives used, iodine was found to be superior to others to afford **2** in high yield (entries 10, 19–21). The results with other mesoporous silicas, MCM-41,[8] HMS,[9] and 10%Ti-HMS,[10] showed FSM-16 to be better as a promoter of the oxidation (entries 22–24).[11]

Other double bonds, which are conjugated to an aromatic nucleus, were oxidatively cleaved to the corresponding carboxyl groups exclusively (Table 2).[6] 4-*tert*-Butylstyrene (**1**), 4-methylstyrene (**3**) and 4-methoxystyrene (**7**), which possess an electron-donating group at the aromatic nucleus, afforded the corresponding benzoic acids (**2**, **4**, **8**) in higher yield than that of styrene (**5**) (entries 1–4). 4-Nitrostyrene (**9**), which possesses an electron-withdrawing group, was less reactive than **5**, and afforded 4-nitrobenzoic acid (**10**) in moderate yield (entry 5). Although the size of the aromatic nucleus of the substrates does not exert any influence on the reactivity, the substituent at the α- or β-position of the double bonds retarded the reaction: 2-vinylnaphthalene (**11**), which possesses a large aromatic nucleus, also gave 2-naphthoic acid (**12**) in 69% yield; however, α-methylstyrene (**13**), β-methylstyrene (**15**), 1,1-diphenylethylene (**16**) and stilbene (**18**), which possess di-substituted double bonds, were found to afford the corresponding products (**14**, **6**, **17**) in low yield or the starting material was recovered intact even after 48 h, respectively (entries 6–10). A detailed comparison of the results when using **13** and **16**, or **15** and **18** as substrates suggests that the double bonds are oxidatively cleaved at the active sites which exist in the pore of FSM-16. A nonconjugated olefin, 1-dodecene (**19**), was intact under this condition (entry 11).

Synlett 2002, No. 3, 04 03 2002. Article Identifier:
1437-2096,E;2002,0,03,0522,0524,ftx,en;Y24501ST.pdf.

ISSN 0936-5214

Table 1 Study of Reaction Conditions for Oxidative Cleavage of 4-*tert*-Butylstyrene (**1**) with FSM-16



1 (50 mg) **2**

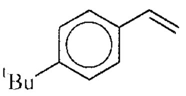
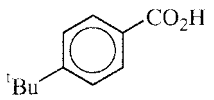
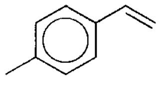
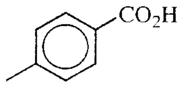
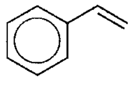
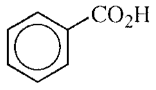
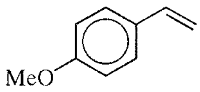
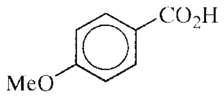
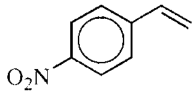
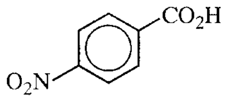
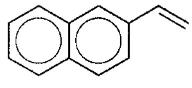
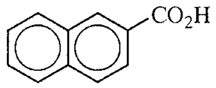
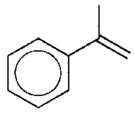
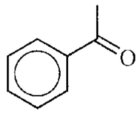
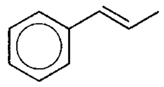
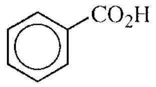
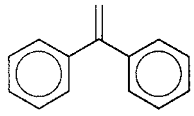
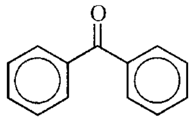
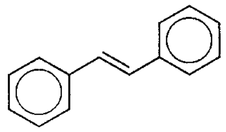
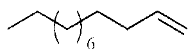
Entry	Solvent	Silica	Additive (equiv)	Recovery of **1** (%)	Yield of **2** (%)
1	Hexane	FSM-16	I_2 (0.3)	–	45
2	Benzene	FSM-16	I_2 (0.3)	–	21
3	MeCN	FSM-16	I_2 (0.3)	–	11
4	THF	FSM-16	I_2 (0.3)	–	40
5	*t*-BuOMe	FSM-16	I_2 (0.3)	–	61
6	MeOH	FSM-16	I_2 (0.3)	–	29
7	CH_2Cl_2	FSM-16	I_2 (0.3)	–	trace
8	DMF	FSM-16	I_2 (0.3)	58	0
9	Acetone	FSM-16	I_2 (0.3)	61	0
10	*i*-Pr_2O	FSM-16	I_2 (0.3)	–	82
11	*i*-Pr_2O	FSM-16	I_2 (0.3)	–	87[a]
12	*i*-Pr_2O	FSM-16	I_2 (0.3)	77	0[b]
13	*i*-Pr_2O	FSM-16	I_2 (0.3)	64	0[c]
14	*i*-Pr_2O	–	I_2 (0.3)	trace	19
15	*i*-Pr_2O	FSM-16	–	71	trace
16	*i*-Pr_2O	FSM-16	I_2 (0.1)	38	23
17	*i*-Pr_2O	FSM-16	I_2 (0.5)	–	50
18	*i*-Pr_2O	FSM-16	I_2 (1.0)	–	14
19	*i*-Pr_2O	FSM-16	Br_2 (0.3)	66	9
20	*i*-Pr_2O	FSM-16	CsI (0.3)	28	12
21	*i*-Pr_2O	FSM-16	CsI (1.0)	–	61
22	*i*-Pr_2O	MCM-41	I_2 (0.3)	8	39
23	*i*-Pr_2O	HMS	I_2 (0.3)	4	54
24	*i*-Pr_2O	10% Ti-HMS	I_2 (0.3)	–	63

[a] The reaction was carried out for 48 h.
[b] The reaction was carried out in the dark.
[c] The reaction was carried out under a flow of argon.

Furthermore, the distinction between the double bonds which are conjugated with an aromatic nucleus and non-conjugated bonds is possible under the same reaction conditions. Scheme 2 shows the result for oxidation of a mixture of **1** and **19**, and **1** was selectively oxidized to **2** and **19** was recovered intact.

Table 2 Oxidative Cleavage of Double Bonds with FSM-16

$$\textbf{substrate}\ (50\ \mathrm{mg})\ \xrightarrow[i\mathrm{Pr_2O}\ (5\ \mathrm{ml}),\ \mathrm{r.t.,\ 48\ h}]{\mathrm{FSM\text{-}16\ (100\ mg)},\ \mathrm{I_2\ (0.3\ equiv.)},\ h\nu}\ \textbf{product}$$

Entry	Substrate	Product (% yield)
1	 **1**	 **2** (87)
2	 **3**	 **4** (81)
3	 **5**	 **6** (68)
4	 **7**	 **8** (71)
5	 **9**	 **10** (46)
6	 **11**	 **12** (69)
7	 **13**	 **14** (24)
8	 **15**	 **6** (33)
9	 **16**	 **17** (12)[a]
10	 **18**	no reaction[b]
11	 **19**	no reaction[c]

[a] 1,1-Diphenylethylene (**16**) was recovered in 64% yield.
[b] Stilbene (**18**) was recovered in 88%.
[c] 1-Dodecene (**19**) was recovered in 57% yield.

$$\begin{array}{l}\mathbf{1}\ (50\ \text{mg})\\ +\\ \mathbf{19}\ (50\ \text{mg})\end{array} \xrightarrow[i\text{Pr}_2\text{O (10 ml), 48 h}]{\substack{\text{FSM-16 (200 mg)}\\ \text{I}_2\ \text{(0.3 equiv.), h}\nu\ \text{(400 W)}}} \begin{array}{c}\mathbf{2}\ (74\ \%)\\ +\\ 60\ \%\ \text{of}\ \mathbf{19}\\ \text{was recovered}\end{array}$$

Scheme 2

The promoter FSM-16 was found to be a recyclable photocatalyst. Thus, the recovered FSM-16, which was dried at room temperature for 2 h under reduced pressure, showed no loss of activity for the reaction after being used three times (Table 3).

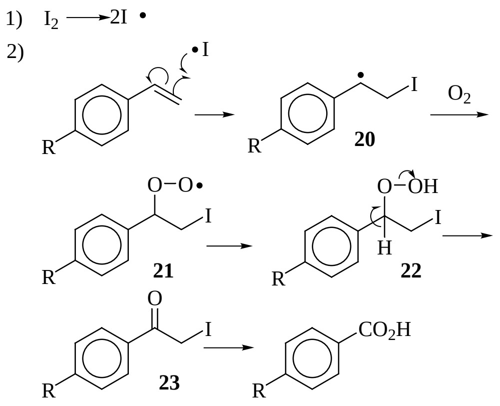
Table 3 Recycle of FSM-16

$$\begin{array}{c}\mathbf{1}\\ (50\ \text{mg})\end{array} \xrightarrow[i\text{Pr}_2\text{O (5 ml), r.t., 36 h}]{\substack{\text{FSM-16}\\ \text{I}_2\ \text{(0.3 equiv.)}, h\nu}} \mathbf{2}$$

Cycle of FSM-16	1st	2nd	3rd
Yield (%) of **2**	80	84	81

Although the mechanism of the interaction between the substrate and the active site on the pore walls of FSM-16 and the reasons for the promoting effect of a catalytic amount of iodine are not yet clear, Scheme 3 shows a possible path by considering both the lack of promoting effect without oxygen in this reaction and our previous study for oxidation with FSM-16.[4] Benzyl radical species **20** is generated by addition of an iodine radical, which is formed under photoirradiation, to the double bond. Radical species **20** traps molecular oxygen in air to afford **21**, and, furthermore, hydroperoxide **22** is thought to be formed by abstraction of the hydrogen atom from a hydrogen source such as *i*-Pr_2O or FSM-16. We believe α-iodo carbonyl compound **23** is a key intermediate, since 4-*tert*-butylphenacyl iodide (**23**, R = *t*-Bu) was detected by NMR as a by-product in the course of the reaction when using **1** as substrate, and **2** was obtained in 62% yield when using 4-*tert*-butylphenacyl iodide as substrate under the same reaction conditions. The intermediate **23** is then transformed to the corresponding carboxylic acid under the conditions, although the details of the transformation are not clear.

In conclusion, we have found a useful method for selective cleavage of double bonds conjugated with an aromatic nucleus with a combination of FSM-16 and catalytic iodine under photoirradiation.



Scheme 3

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(5) A typical procedure follows: In a pyrex tube, a suspension of 4-tert-butylstyrene (**1**, 50 mg), iodine and silica (100 mg) in dry *i*-Pr_2O (5 mL) was stirred, and irradiated externally at room temperature with a 400-W high-pressure mercury lamp under aerobic atmosphere for 36 h. FSM-16 was then filtered off and washed with ethyl acetate, and the filtrate was washed with aq. sodium thiosulfate solution and brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Pure 4-*tert*-butylbenzoic acid (**2**) (46 mg, 82%) was obtained after purification by preparative TLC.

(6) The reaction will be completed in a much shorter reaction time than that indicated in the table with a new 400-W high-pressure mercury lamp, since the lamp, we used, is thought to be deteriorated: it had been used for a long time (14000 hrs) before this study. Product **2**, for example, was afforded in 80% yield for 18 h reaction with a new lamp when **1** was used as starting material..

(7) The unit cell dimension of FSM-16 was 45.3 nm. The pore diameter was 2.8 nm, and the specific surface area was 948 m^2/g.

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(11) The pore walls of FSM-16 with higher stability than MCM-41 will suppress the conversion of strained siloxane bridges, which are proposed to be the active sites for photo reaction, into inactive unstrained bridges, see: Inaki, Y.; Yoshida, H.; Kimura, K.; Inagaki, S.; Fukushima, Y.; Hattori, T. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5293.