

Synthesis and Application of New Phenyl-Functionalized Zeolites as Protection Against Radical Bromination at the Benzylic Position

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Abstract: New zeolites functionalized with phenyl group have been synthesized from phenyltriethoxysilane and/or tetraethylorthosilicate with dodecylamine as a template at room temperature. These zeolites have proved to have an ability to protect the benzylic position against radical bromination. 4-Chloromethylstyrene was brominated at the double bond selectively and the benzylic position was intact under irradiation with visible light in the presence of phenyl-functionalized zeolites, although without the zeolite, the both sites were brominated.

The chemistry of zeolites has long been studied.¹ In recent years especially syntheses of new type of zeolites have been reported by many workers.² The main reason for development of zeolites is that they are defined as one of the microporous crystal substances, which is easier to control in structure,^{3a} chemical character, and composition of pore^{3b} than microporous amorphous substances such as silica gel and alumina. Taking advantage of acidic property and shape-selectivity, zeolites have been used for a variety of reactions, such as oxidation,⁴ epoxidation,^{4a,5} bromination,⁶ and C-C bond formation.⁷ Recently several alkyl-functionalized zeolites, so-called hybrid zeolites, also have been reported.^{8,9} Much attention have been focused on organic-inorganic hybrid zeolites taking advantage of two fundamental properties. First, inorganic framework provides thermal and structural stabilities. Second, organic components endowed the system with a variety of specific chemical functions by modification of organic groups.⁹ Now we report a syntheses of new zeolites which are functionalized by a phenyl group and its inhibitory activity against radical bromination at the benzylic position.

In order to investigate the application of zeolites to a variety of organic reactions, we selected hexagonal mesoporous silica (HMS) as an agreeable zeolite for our purposes because it possesses larger pore size for our target molecules than other zeolites, and is synthesized easily from commercially available tetraethylorthosilicates (**1**) at room temperature.^{2b} Phenyl groups can be introduced into the framework of zeolite by hybridizing phenyltriethoxysilane (**2**) or benzyltriethoxysilane (**3**) in the starting materials (Figure 1). The zeolite syntheses have been attempted in the presence of dodecylamine as a template, in water with ethanol as a co-solvent,^{2b} which improved the template solubility. Typical procedure is as follows; To a foamy solution of dodecylamine (4.16 g, 22.5 mmol) and 1N-HCl aq. (1.6 ml, 1.6 mmol) in water (32 ml) was added at room temperature an ethanol solution (32 ml) of **2** or **3** (83.2 mmol) and various molar equivalents of **1** under vigorous stirring. After the resulting mixture was aged at ambient temperature for 18 hr, a white precipitate was obtained. Filtration of the precipitate followed by washing with ethanol several times and drying at 100 °C under vacuum gave a white powder, which is called tentatively Ph-HMS (1:0) (**4**), Ph-HMS (1:1) (**5**), PhHMS (1:5) (**6**), Ph-HMS (1:10) (**7**), and Bn-HMS (1:2) (**8**) (Table 1) respectively. The numbers in the parentheses show the molar equivalent ratio of silicates used **2** to **1**, or **3** to **1**.

Generally zeolites have shape-selectivity due to their pore size. Although the structure of a series of Ph-HMS and Bn-HMS are not clear, they are expected to possess characteristic pore size like usual

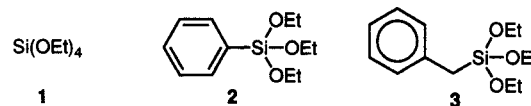


Figure 1

Table 1

R-Si(OEt) ₃ + Si(OEt) ₄		Laurylamine, HCl EtOH - H ₂ O, r.t., 24 hr		R-HMS
R-Si(OEt) ₃	R-Si(OEt) ₃ : Si(OEt) ₄	Zeolite		
2	1 : 0	Ph-HMS (1:0)	4	
2	1 : 1	Ph-HMS (1:1)	5	
2	1 : 5	Ph-HMS (1:5)	6	
2	1 : 10	Ph-HMS (1:10)	7	
3	1 : 2	Bn-HMS (1:2)	8	

zeolites. So we employed the zeolites prepared in bromination of toluene to compare the shape-selectivity of Ph-HMS and Bn-HMS with that of other zeolites. It was reported that bromination of toluene (**9**) with NaY zeolite at room temperature afforded 98% yield of *p*-bromotoluene due to its shape selectivity.^{6a} In the present experiment Ph-HMS (1:0) (**4**) was found to inhibit not only aromatic bromination but also radical bromination at benzylic position of toluene (**9**) (Table 2). Thus, in the presence of Ph-HMS (**4**), benzylbromide (**10**), a brominated product at benzylic position of toluene (**9**), was obtained in only 18% yield¹¹ under irradiation with visible light using 60 W fluorescent lamp, whereas the total yield of brominated products at benzylic position (**10** and **11**) is about 100% under the conditions without Ph-HMS (**4**) (Table 2).¹² Remarkable chemoselectivity was observed in bromination of 4-methylstyrene (**12**) and 4-chloromethylstyrene (**16**) using Ph-HMS (**4**) as shown in Table 3 and 4. Presence of PhHMS (**4**) affected the reaction courses of 4-methylstyrene (**12**) on treatment with 2.1 equiv. of bromine to provide mainly addition product (**13**), whereas without Ph-HMS (**4**), 4-bromomethyl-1',2'-dibromoethylbenzene (**14**) which were produced by both olefinic bromination and substitution reaction of benzylic position, was obtained in a good yield (82%) in addition to a small amount of a tetrabrominated compound (**15**). In a case of

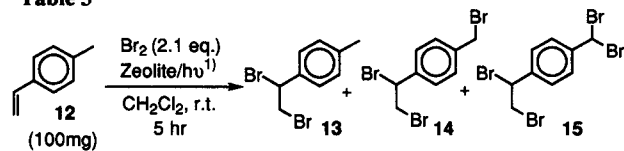
Table 2

Zeolite	Amount (mg)	Time (hr)	Yield (%)	
			10	11
4	100	24 ¹⁾	0	0
4	100	2 ²⁾	18	0
-	-	2 ²⁾	86	11

1) Under dark. 2) Irradiated with 60 W fluorescent lamp

(18) exclusively under the usual conditions, benzylic bromination was completely inhibited in the presence of Ph-HMS (4) to give only dibromide (17), an olefinic bromination product. Hybrid zeolites, Ph-HMS (5, 6, 7) and Bn-HMS (8) afforded almost same results as shown in Table 4. On the other hand it is worth noting that the original zeolite HMS promoted radical bromination at the benzylic position of 12 and 16 (Table 3, 4).

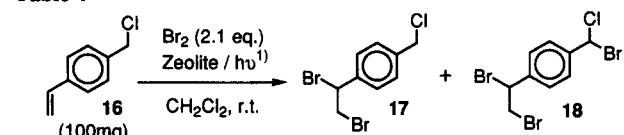
Table 3



Zeolite	Amount (mg)	Yield (%)		
		13	14	15
-	-	10	82	8
HMS	100	0	69	22
4	100	68	31	0
4	200	73	27	0
4	300	77	23	0

1) Irradiated with 60 W fluorescent lamp

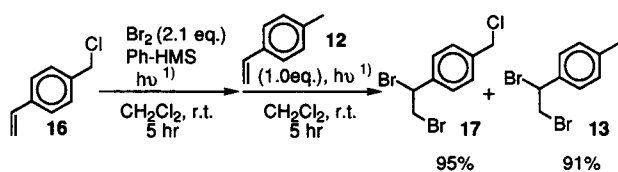
Table 4



Zeolite	Amount (mg)	Time (hr)	Yield (%)	
			17	18
-	-	2	0	84
HMS	100	5	complex mixture	
4	100	5	100	0
5	100	5	97	0
6	100	5	100	0
7	100	5	84	0
8	100	5	100	0

1) Irradiated with 60 W fluorescent lamp

Bromine proved to be not consumed by the zeolites from the results of crossover experiment as shown in Scheme 1. At first 4-chloromethylstyrene (16) was treated with a 2.1 equiv. of bromine and Ph-HMS (4) under irradiation for 5 hr, the period of which is long enough to complete both the addition and the substitution reaction of 16 with bromine in the absence of Ph-HMS. Then another substrate 12 (1.0 equiv.) was added to the reaction mixture and the whole was allowed to react for another 5 hr. After usual work-up, the products obtained were only 17 and 13, which were not the products formed by attack of bromine at the benzylic position. Inverse treatment of 12 and 16 afforded almost the same result. These results show that Ph-HMS (4) does not consume the bromine, but "protects" benzylic position against radical bromination. It can be presumed that non-bonding interaction



1) Irradiated with 60 W fluorescent lamp

Scheme 1

between phenyl group of the zeolite and benzyl group of substrates, or interaction between the pore of the zeolite and benzyl group are involved in the course of this reaction. Further investigation of the detailed structure of Ph-HMS, the mechanism of protection of benzylic position, and the utilities of these zeolites for other organic reactions are in progress in our laboratory.

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- 10) Ph-HMS (1:0) (**4**) has proved to be dissolved in chloroform, dichloromethane, ethyl acetate, benzene, toluene, and DMF. On the other hand methanol and ethanol have proved to be poor solvents for the zeolite.
- 11) Unreacted toluene was evaporated through work-up because of its low boiling point.
- 12) General procedure: To a dried dichloromethane solution (5 ml) of the substrate (100 mg) and the zeolite (100 mg), bromine (2.1 eq.) was added under stirring at room temperature. The mixture was stirred for 5 hr under irradiation with visible light using 60 W fluorescent lamp. The reaction mixture was diluted with dichloromethane and washed with water, sat. sodium thiosulfate solution, and brine. After drying over sodium sulfate and concentration, the residue was purified by silica gel chromatography to give pure brominated compounds.