Chinese Chemical Letters Vol. 16, No. 4, pp 527-530, 2005
http://www.imm.ac.cn/journal/ccl.html

Benzylation of Aromatic Compounds with Benzyl Chloride Catalyzed by Nafion/SiO_2 Nanocomposite Catalyst

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Abstract: In the presence of Nafion/SiO_2 nanocomposite catalyst, the benzylation of aromatic compounds with benzyl chloride proceeded to afford diphenylmethane derivatives in high yields. The catalyst showed high catalytic activity not only for electron-rich aromatic compounds, but also for electron-poor aromatic compounds. Under identical conditions, the self-benzylation of benzyl chloride, and dibenzylation and/or multi-benzylation of aromatic compounds were negligible.

Keywords: Benzylation, aromatic compound, benzyl chloride, nafion/SiO_2 nanocomposite.

Diphenylmethane and substituted diphenylmethane are important compounds for synthesis chemistry as well as industrial chemistry. These compounds are easily synthesized by the benzylation of aromatic compounds with benzyl chloride or benzyl alcohol catalyzed by homogeneous acid catalysts, such as $AlCl_3$, $FeCl_3$, H_2SO_4, HF and BF_3. However, these catalytic systems are highly corrosive, and usually proceed with low selectivity. In addition, they are less satisfactory from the environmental point of view, due to formation of a large number of waste materials during separation of the products from reaction mixture. Hence, recently, various solid catalysts have been employed for this type of reaction[1].

In our laboratory, the high surface area Nafion/SiO_2 nanocomposites, which have different Nafion contents (5 ~ 20 wt %) with nano-sized Nafion resin particles have been prepared. It has been found that the Nafion/SiO_2 nanocomposites show the same or higher catalytic activity than Nafion in the reactions of alkylation of benzene, dimerization of 2-methyl styrene and the synthesis of α-tocopherol[2]. Herein we wish to report the results of the application of the prepared Nafion/SiO_2 nanocomposites as catalyst in the benzylation of aromatic compounds with benzyl chloride.

The benzylation was carried out in a mixture of benzyl chloride (1.2 mmol), an excess of aromatic compound (*ca*. 24.0 mmol) and Nafion/SiO_2 (13 wt % of Nafion, 100 mg, acid amount ~0.011 mmol) at 120 °C. The reaction progress and yield were monitored and determined by GC using an internal standard. In order to minimize the

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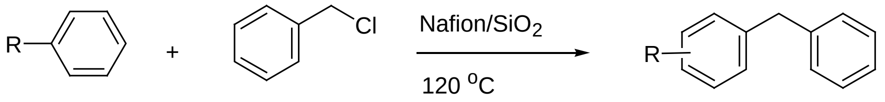
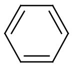
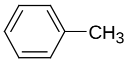
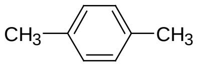
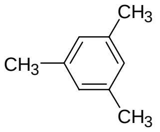
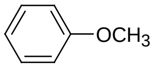
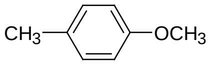
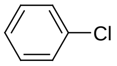
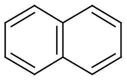
self-benzylation of benzyl chloride, an excess of aromatic compounds are used (aromatic compound/benzyl chloride = 20/1 molar). It was confirmed that, under the identical reaction conditions, the self-benzylation of benzyl chloride was negligible, and the yields of the dibenzylation and/or multi-benzylation was less than 5 % as determined by GC and GC-MS.

As can be seen from **Table 1**, the rate of benzylation was dependent on the nature of the aromatic compounds employed. We first examined the reaction of benzene with benzyl chloride at 80 °C, the reaction was very slow and gave only 20 % of diphenylmethane after 24 h. In a closed system, heating the reaction mixture at 120 °C (oil bath temperature) for 10 h resulted in the formation of diphenylmethane in 30 % yield with the recovery of benzyl chloride (entry 1). These results indicated that a higher temperature is necessary to achieve reasonable yield of the benzylated products. Therefore, all the other reactions were performed at 120 °C.

Table 1 Nafion/SiO_2-catalyzed benzylation of aromatics with benzyl chloride[a]



entry	aromatics	time (h)	conversion	yield (%)b	ratio of *o-: m-: p-* isomerc
1		10	30	29	—
2		1.5	98	92(83)	45:8:47
3		0.75	100	96(84)	—
4		0.5	100	95(90)	—
5		8.0	96	94(78)	47:<1:52
6		8.0	98	98(85)	*d*
7		1.0	100	99(92)	38:<1:61
8		0.5	100	99(86)	*e*

[a] Reactions were performed using benzyl chloride (1.2 mmol), aromatics (ca. 24.0 mmol), and Nafion/SiO_2 (13 wt % of Nafion, 100 mg) at 120 °C. [b] Isolated yield, the number in the parentheses is the GC yield. [c] Ratio in reaction mixture confirmed by GC and ^1H NMR. [d] 2-Benzyl-4-methylanisole : 3-Benzyl-4-methylanisole = 82 : 18. [e] a : b = 67 : 33.

The benzylation of toluene, *p*-xylene and mesitylene proceeded with the trend: mesitylene > *p*-xylene > toluene, and afforded the benzylated products in high yields (entries 2-4). In the case of toluene, the reaction gave predominantly *ortho* and *para*-substituted products. For other electron-rich aromatic compounds such as anisole and 4-methylanisole, to achieve the high yields of benzylated products, a prolonged reaction time was required (entries 5-6).

In the present catalytic system, the aromatic compounds substituted by electron-withdrawing group, such as nitro, methoxycarbonyl and chloro show remarkably different reactive activity. The reactions of nitrobenzene, methyl benzoate with benzyl chloride were very sluggish, after 10 h at 120 ^{o}C, very low yields of benzylated products (<10%) were obtanied. However, chlorobenzene showed unexpected high reactivity to give the corresponding benzylated products in 99 % GC yield after 1 h. In this case, the reaction almost afforded the *ortho* and *para*-substituted products in a ratio of 38 : 61 (entry 7).

The benzylation reaction of naphthalene also proceeded readily to give α, β-benzylated products in nearly quantitative yield with the α, β-benzylated products in a ratio of 67 : 33 (entry 8).

In addition, the catalytic activity of the recovered catalyst has also been examined. After the reaction (as indicated in **Table 1**, entry 3), the reaction mixture (organic phase) was separated carefully by syringe. The residue (catalyst) was washed with diethyl ether twice, and then dried at 120 ^{o}C in vacuum for 1 h. To this residue, benzyl chloride (1.2 mmol) and *p*-xylene (*ca*. 24.0 mmol) were added, and then the resulting mixture was heated at 120 ^{o}C for 0.75 h with stirring. On the basis of the GC analysis of the reaction mixture, the conversion of *p*-xylene and the yield of the benzylated product were the same as those shown in **Table 1**, entry 3. These results indicated that Nafion/SiO_2 could be easily recovered and reused without decrease of the catalytic activity.

General procedure: In a round-bottomed flask (25.0 mL) equipped with a condenser and a magnetic stirrer, a mixture of benzyl chloride (1.2 mmol), aromatic compound (*ca*. 24.0 mmol) and Nafion/SiO_2 (13 wt % of Nafion, 100 mg, acid amount ~0.011 mmol) was stirred at 120 ^{o}C for the indicated time as shown in **Table 1**. $C_{16}H_{34}$ or $C_{18}H_{38}$ was added to the reaction mixture as internal standard material for GC analysis. After removal of the catalyst by filtration and concentration of organic solution, the residue was subjected to purify by silica gel chromatography to afford benzylated compounds. All of the benzylated compounds are known compounds, and their structures were identified by GC-MS and compared with the authentic samples.

Acknowledgments

This work was financially supported by the Beijing Research Institute of Petroleum Processing.

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Received 29 March, 2004