This article was downloaded by: [Istanbul Universitesi Kutuphane ve Dok]
On: 21 December 2014, At: 22:34
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Efficient and Mild Iron-Catalyzed Direct Allylation of Benzyl Alcohols and Benzyl Halides with Allyltrimethylsilane

Jie Han [a] , Zili Cui [a] , Jianguo Wang [a] & Zhongquan Liu [a]
[a] Institute of Organic Chemistry, Gannan Normal University, Ganzhou, China and Lanzhou University , Lanzhou, China

Published online: 17 Jun 2010.

To cite this article: Jie Han , Zili Cui , Jianguo Wang & Zhongquan Liu (2010) Efficient and Mild Iron-Catalyzed Direct Allylation of Benzyl Alcohols and Benzyl Halides with Allyltrimethylsilane, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:14, 2042-2046, DOI: 10.1080/00397910903219393

To link to this article: http://dx.doi.org/10.1080/00397910903219393

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Synthetic Communications®, 40: 2042–2046, 2010

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903219393

Taylor & Francis
Taylor & Francis Group

EFFICIENT AND MILD IRON-CATALYZED DIRECT ALLYLATION OF BENZYL ALCOHOLS AND BENZYL HALIDES WITH ALLYLTRIMETHYLSILANE

Jie Han, Zili Cui, Jianguo Wang, and Zhongquan Liu
Institute of Organic Chemistry, Gannan Normal University, Ganzhou, China and Lanzhou University, Lanzhou, China

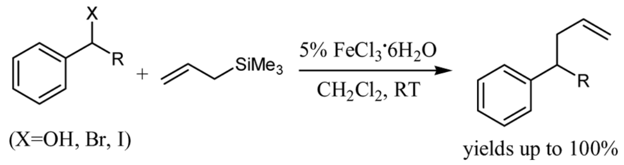
An efficient and mild iron-catalyzed direct allylation of benzyl alcohols and benzyl halides with allyltrimethylsilane has been developed. The present reaction would provide an excellent alternative to published methods because of its excellent yields, sustainable catalyst, and mild conditions.

Keywords: Allylation; benzyl alcohols; benzyl halides; iron catalysis

The development of direct carbon–carbon (C–C) bond construction that uses low-cost, environmentally benign, and sustainable catalysts is a critical challenge for organic chemists. Recently, catalytic systems using iron as the active catalyst have received great attention, and some efficient iron-catalyzed systems have been developed for C–C couplings.[1] Herein, we report an efficient and mild iron-catalyzed direct allylation of benzyl alcohols and benzyl halides with allyltrimethylsilane.

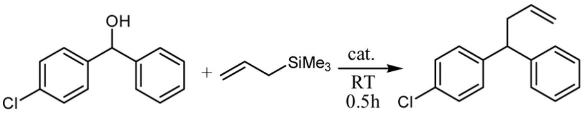
Although few C–C bond constructions using benzyl alcohols have been achieved because of the poor leaving ability of the hydroxide group, it remains very attractive because it would be atom-efficient and environmentally benign, as water is the only by-product.[2] In past years, some efficient methods have been explored to prepare terminal olefins via direct allylation of benzyl alcohols with allyltrimethylsilane using various catalysts, such as BF_3,[3] bis(fluorosulfuryl)imide,[4] $B(C_6F_5)_3$,[5] $InCl_3$,[6] $InBr_3$,[7] $BiCl_3$,[8] $ZrCl_4$,[9] and H-montmorillonite.[10] However, many of these systems suffer from hash reaction conditions[3–5,10] and relatively expensive metal catalysts.[6–9] Therefore, development of more efficient and mild catalysts to promote the direct allylation of benzyl alcohols remains attractive. We successfully accomplished an efficient and mild catalytic allylation of benzyl alcohols and halides with allyltrimethylsilane by using 5 mol% of $FeCl_3 \cdot 6H_2O$ as the active catalyst (Scheme 1, Table 1). To the best of our knowledge, this is the first example of an iron-catalyzed allylation of benzyl alcohols and halides with allylsilane. (It puzzled us that a very low yield (5%) of the allylated product was obtained using benzhydrol

Received March 26, 2009.
Address correspondence to Zhongquan Liu, Institute of Organic Chemistry, Gannan Normal University, Ganzhou 341000, China. E-mail: liuzhongquan@yahoo.cn



Scheme 1. Iron-catalyzed allylation of benzyl alcohols and halides with allyltrimethylsilane.

Table 1. Optimization of the typical reaction conditions[a]



Entry	Catalyst (mol%)	Solvent	Isolated yield (%)
1	$FeCl_3$ (5)	CH_2Cl_2	100
2	$FeCl_3 \cdot 6H_2O$ (5)	CH_2Cl_2	100 100^b 84^c
3	$Fe_2(SO_4)_3$ (5)	CH_2Cl_2	0
4	$FeCl_2$ (5)	CH_2Cl_2	0
5	$CuBr_2$ (5)	CH_2Cl_2	0
6	CuBr (5)	CH_2Cl_2	0
7	$FeCl_3 \cdot 6H_2O$ (2)	CH_2Cl_2	94
8	$FeCl_3 \cdot 6H_2O$ (1)	CH_2Cl_2	86
9	$FeCl_3 \cdot 6H_2O$ (5)	$CHCl_3$	0
10	$FeCl_3 \cdot 6H_2O$ (5)	DCE	60
11	$FeCl_3 \cdot 6H_2O$ (5)	CH_3CN	0
12	$FeCl_3 \cdot 6H_2O$ (5)	H_2O	0
13	$FeCl_3 \cdot 6H_2O$ (5)	Hexane	0
14	$FeCl_3 \cdot 6H_2O$ (5)	THF	0

[a] Reaction conditions: 1-phenyl-1-p-chlorophenyl methanol (0.5 mmol), allyltrimethylsilane (1.0 mmol), rt, 0.5 h.

[b] Alcohol/allylsilane = 1:3.

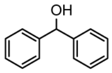
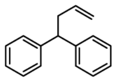
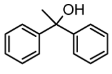
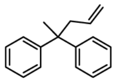
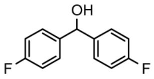
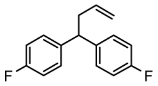
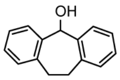
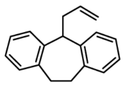
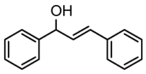
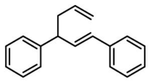
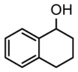
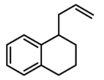
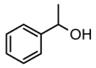
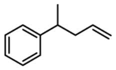
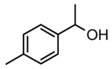
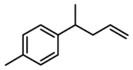
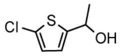
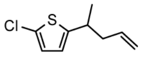
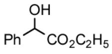
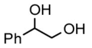
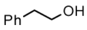
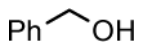
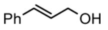
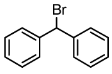
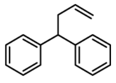
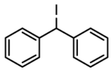
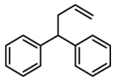
[c] Alcohol/allylsilane = 1:1.

and allyltrimethylsilane catalyzed by 5% $FeCl_3$, according to Ref. 8. However, we obtained nearly quantitative yield of the desired product by using 5% $FeCl_3$ under a similar condition.)

EXPERIMENTAL

For the initial research, we select 1-phenyl-1-*p*-chlorophenyl methanol and allyltrimethylsilane as standard substrates to optimize suitable conditions for this substitution reaction (Table 1). The desired allylation product was obtained in quantitative yield using 5 mol% of anhydrous $FeCl_3$ at room temperature in CH_2Cl_2 (entry 1). It is interesting that 100% isolated yield of the product was also obtained by using 5 mol% of $FeCl_3 \cdot 6H_2O$ as catalyst (entry 2). The yield of product decreased

Table 2. Allylation of benzyl alcohols and halides with allyltrimethylsilane[a]

Entry	Benzyl alcohols or halides	Products	Time (min)	Isolated yield (%)
1			30	98
2			30	80
3			30	94
4			30	100
5			30	71
6			60	88
7			60	25
8			40	84
9			30	95
10		—	180	0
11		—	180	0
12		—	180	0
13		—	180	0
14		—	50	Mixture
15			30	93
16			30	91

[a] Reaction conditions: benzyl alcohol or benzyl bromide (0.5 mmol), allyltrimethylsilane (1.0 mmol), 5 mol% $FeCl_3 \cdot 6H_2O$ (0.025 mmol), CH_2Cl_2, rt.

to 84% while the reaction was carried out with equal amount of alcohol and silane. However, other iron salts and copper salts were inactive to this reaction (entries 3–6). Decrease or increase of the catalyst dosage was less efficient than 5 mol% (entries 7 and 8). Further investigation of solvent effect showed that CH_2Cl_2 is a more effective solvent (entries 9–14).

Various alcohols have been tested as substrates for the allylation reaction (Table 2). It is seen from Table 2 that diaryl methanols gave good to excellent, even quantitative, yields of the products (entries 1–4). 1,3-Diphenyl-allyl alcohol also gave a good yield of the corresponding allylation product (entry 5). An excellent yield was obtained by using 1,2,3,4-tetrahydro naphthalen-1-ol as the substrate (entry 6). 1-Phenyl ethanol gave a very poor yield of the product (entry 7), whereas 1-*p*-methyl-phenyl ethanol gave 84% isolated yield (entry 8). 1-(5-Chloro-thiophen-2-yl)-ethanol also gave excellent yield of the desired product (entry 9). However, hydroxy-phenyl-acetic acid ethyl ester (entry 10), 1-phenyl-ethane-1,2-diol (entry 11), 2-phenyl-ethanol (entry 12), and phenylmethanol (entry 13) were inactive in this system. 3-Phenyl-prop-2-en-1-ol gave a mixture under the condition in entry 14. It is noteworthy that benzyl halides such as bromo-diphenyl-methane and iodo-diphenyl-methane also gave excellent yields of the allylation products (entries 15 and 16).

In conclusion, this work demonstrates an efficient and mild iron-catalyzed allylation of benzyl alcohols and halides with allyltrimethylsilane. Compared with the systems reported before, the present method provides a better alternative because of its sustainable catalyst and mild conditions. Extension of this system to other substrates is under way in our laboratory.

ACKNOWLEDGMENT

We thank Gannan Normal University for financial support.

REFERENCES

1. For recent reviews of iron-catalyzed transformations, see (a) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. Iron-catalyzed reactions in organic synthesis. *Chem. Rev.* **2004**, *104*, 6217; (b) Enthaler, S.; Junge, K.; Beller, M. Sustainable metal catalysis with iron: From rust to a rising star? *Angew. Chem. Int. Ed.* **2008**, *47*, 3317; (c) Sherry, B. D.; Fürstner, A. The promise and challenge of iron-catalyzed cross coupling. *Acc. Chem. Res.* **2008**, *41*, 1500; For select recent examples of C–C bond formation catalyzed by iron, see (a) Martin, R.; Fürstner, A. Cross-coupling of alkyl halides with aryl Grignard reagents catalyzed by a low-valent iron complex. *Angew. Chem. Int. Ed.* **2004**, *43*, 3955; (b) Iovel, I.; Mertins, K.; Kischel, J.; Zapf, A.; Beller, M. An efficient and general iron-catalyzed arylation of benzyl alcohols and benzyl carboxylates. *Angew. Chem. Int. Ed.* **2005**, *44*, 3913; (c) Lu, Z.; Chai, G.; Ma, S. Iron-catalyzed highly regio- and stereoselective conjugate addition of 2,3-allenoates with Grignard reagents. *J. Am. Soc. Chem.* **2007**, *129*, 14546; (d) Jana, U.; Biswas, S.; Maiti, S. A simple and efficient $FeCl_3$-catalyzed direct alkylation of active methylene compounds with benzylic and allylic alcohols under mild conditions. *Tetrahedron Lett.* **2007**, *48*, 4065; (e) Wang, B.; Xiang, S.; Sun, Z.; Guan, B.; Hu, P.; Zhao, K.; Shi, Z. Benzylation of arenes through $FeCl_3$-catalyzed Friedel–Crafts reaction via C–O activation of benzyl ether. *Tetrahedron Lett.* **2008**, *49*, 4310; (f) Liu, Z.; Wang, J.; Han, J.; Zhao, Y.; Zhou, B. An efficient and mild iron-mediated synthesis of alkenyl

halides via direct C–C bond formation of benzyl alcohols and aryl alkynes. *Tetrahedron Lett.* **2009**, *50*, 1240; (g) Liu, Z.; Wang, J.; Zhao, Y.; Zhou, B. A mild and efficient iron-catalyzed synthesis of alkenyl halides via direct addition of benzyl halides to arylalkynes. *Adv. Synth. Catal.* **2009**, *351*, 371.

2. (a) Dau-Schmidt, J. P.; Mayr, H. Relative reactivities of alkyl chlorides under Friedel–Crafts conditions. *Chem. Ber.* **1994**, *127*, 205; (b) Kabalka, G. W.; Yao, M.; Borella, S.; Wu, Z. Substitution of benzylic hydroxyl groups with vinyl moieties using vinylboron dihalides. *Org. Lett.* **2005**, *7*, 2865; (c) Kabalka, G. W.; Yao, M.; Borella, S. Generation of cations from alkoxides: Allylation of propargyl alcohols. *J. Am. Chem. Soc.* **2006**, *128*, 11320; (d) Liu, Y.; Liu, L.; Wang, Y.; Han, Y.; Wang, D.; Chen, Y. Calix[*n*]arene sulfonic acids bearing pendant aliphatic chains as recyclable surfactant-type Brønsted acid catalysts for allylic alkylation with allyl alcohols in water. *Green Chem.* **2008**, *10*, 635.
3. Cella, J. A. Reductive alkylation/arylation of arylcarbinols and ketones with organosilicon compounds. *J. Org. Chem.* **1982**, *47*, 2125.
4. Kaur, G.; Kausik, M.; Trehan, S. Bis(fluorosulfuryl)imide: A Brønsted acid catalyst for the coupling of allylic and benzylic alcohols with allyltrimethylsilane. *Tetrahedron Lett.* **1997**, *38*, 2521.
5. Rubin, M.; Gevorgyan, V. $B(C_6F_5)_3$-catalyzed allylation of secondary benzyl acetates with allylsilanes. *Org. Lett.* **2001**, *3*, 2705.
6. (a) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. Direct substitution of the hydroxy group in alcohols with silyl nucleophiles catalyzed by indium trichloride. *Angew. Chem. Int. Ed.* **2004**, *43*, 1414; (b) Saito, T.; Nishimoto, Y.; Yasuda, M.; Baba, A. Direct coupling reaction between alcohols and silyl compounds: Enhancement of Lewis acidity of Me_3SiBr using $InCl_3$. *J. Org. Chem.* **2006**, *71*, 8516.
7. Kim, S. H.; Shin, C.; Pai, A. N.; Koh, H. K.; Chang, M. H.; Chung, B. Y.; Cho, Y. S. $InBr_3$-catalyzed deoxygenative allylation of benzylic and allylic alcohols and acetates with allyltrimethylsilane. *Synthesis* **2004**, 1581.
8. De, S. K.; Gibbs, R. A. Bismuth(III) chloride–catalyzed direct deoxygenative allylation of substituted benzylic alcohols with allyltrimethylsilane. *Tetrahedron Lett.* **2005**, *46*, 8345.
9. Sharma, G. V. M.; Reddy, K. L.; Lakshmi, P. S.; Ravi, R.; Kunwar, A. C. Direct c-allylation of aryl-alkyl/glycosyl carbinols: Facile synthesis of c-linked carbo-β^2-/γ^2-/δ^2-amino acids. *J. Org. Chem.* **2006**, *71*, 3967.
10. Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. Nucleophilic substitution reactions of alcohols with use of montmorillonite catalysts as solid Brønsted acids. *J. Org. Chem.* **2007**, *72*, 6006.