Deoxygenative Allylation of Benzyl Acetates and Cinnamyl Alcohols Catalyzed by Molecular Iodine

J. S. Yadav,* B. V. Subba Reddy, A. Srinivas Reddy, and B. Eeshwaraiah
Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad-500 007, India

(Received August 6, 2007; CL-070839; E-mail: yadavpub@iict.res.in)

Benzyl acetates undergo smooth deoxygenative allylation with allyltrimethylsilane in the presence of 10 mol % of molecular iodine under mild conditions to afford the corresponding allyl derivatives in excellent yields and with high selectivity. Cinnamyl alcohols also react readily with allylsilane under similar conditions. The use of molecular iodine makes this method quite simple, more convenient and cost effective.

The stereoselective addition of allylsilanes to aldehydes, referred to as the Sakurai–Hosomi reaction has been recognized as one of the most efficient methods for carbon–carbon bond-forming reaction and has been extensively applied in organic synthesis, especially in natural products synthesis.[1,2] Acid-catalyzed carbon–carbon bonding forming reactions are of great significance in organic synthesis because of their high reactivity, selectivity and mild reaction conditions.[3] Benzyl acetates are well-known carbon electrophiles capable of reacting with various nucleophiles and their ability to undergo nucleophilic substitution reactions contributes largely to their synthetic value.[4,5] In recent years, various methods have been reported using Brønsted acids as well as transitions metals.[6] However, there have been no reports on the allylation of benzyl acetates and cinnamyl alcohols with allyltrimethylsilane using molecular iodine. Recently, molecular iodine has received considerable attention as a readily available and cost-effective reagent for various organic transformations, affording the corresponding products with high selectivity in excellent yields. The mild Lewis acidity associated with iodine has led to its use in organic synthesis using catalytic to stoichiometric amounts.[7]

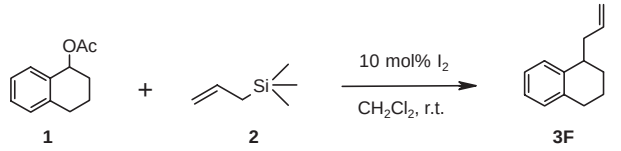
In continuation of our interest on the use of molecular iodine for various organic transformations,[8] we describe herein an efficient method for the allylation of benzyl acetates and cinnamyl alcohols using allyltrimethylsilane with the aid of catalytic amount of molecular iodine. In a preliminary experiment, tetrahydronaphthalen-1-yl acetate (**1**) was treated with allyltrimethylsilane (**2**) in the presence of 10 mol % of molecular iodine. The reaction went to completion within 1.5 h at room temperature and the product 3F was obtained in 82% yield (Scheme 1).

Similarly, a wide range of benzyl acetates underwent smooth allylation with allyltrimethylsilane to afford the corresponding pent-4-en-2-yl benzene derivatives in high yields (Entries **A**–**K**, Table 1). In all cases, the reactions proceed in high yields at room temperature under the influence of 10 mol % of iodine. Interestingly, doubly activated alcohols reacted readily with allyltrimethylsilane to furnish allyl derivatives in excellent yields (Entries **L**–**O**, Table 1, Scheme 2).

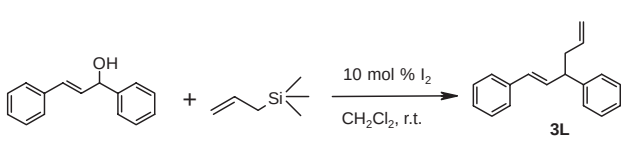
Simple secondary cinnamyl alcohols also participated well in this reaction (Entries **P** and **Q**, Table 1). Unlike benzyl alcohols, cinnamyl alcohols do not require any activating group like acetate to proceed the reaction. However, the allylation of cinnamyl alcohols gave mixture of products arising from γ-substitution as a result of allylic rearrangement, S_N2'-type substitution (Entries **P** and **Q**, Table 1). This method is compatible with esters, amides, halides, aryl alkyl ethers, alkynes, and alkenes present in the molecule. The simple alkyl acetates failed to undergo allylation under the reaction conditions. This method was successful with secondary benzyl acetates and cinnamyl alcohols. As solvent, dichloromethane appeared to give the best results. All products were characterized by ^{1}H, ^{13}C NMR, IR, and mass spectrometry. However, in the absence of catalyst, the reaction did not proceed even after a long reaction time. Interestingly, catalytic amount of TMSI was also found to be equally effective catalyst for this conversion. However, the use of allyltri-*n*-butyltin in place of allyltrimethylsilane did not yield the desired product under these reaction conditions, perhaps because iodine does not interact with allyltri-*n*-butyltin. Thus, the combination of allyltrimethylsilane and iodine could be the method of choice for allylation of benzyl acetates and cinnamyl alcohols.[9] No additives or acidic promoters are required for the reaction to proceed. The catalyst is readily available at low cost and is highly efficient in promoting allylations. Substituted allyltrimethylsilane also reacted well with cinnamyl alcohols to provide methyl-substituted 1,5-dienes (Entries **R** and **S**, Table 1). The scope of this process is illustrated with respect to various benzyl acetates and cinnamyl alcohols and the results are presented in Table 1.[10]

In summary, we have developed a mild, convenient and efficient protocol for the allylation of benzyl acetates and cinnamyl alcohols using a catalytic amount of molecular iodine. In addition to its efficiency, simplicity, and mild reaction conditions, this method provides high yields of products with high selectivity, which makes it a useful and attractive process for the synthesis of allylation of benzyl acetates and cinnamyl alcohols.

ASR and BE thank CSIR, New Delhi for the award of the fellowships.

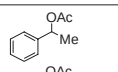
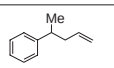
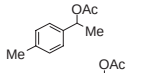
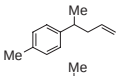
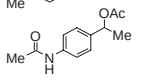
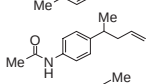
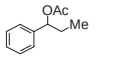
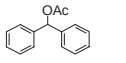
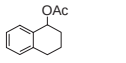
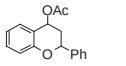
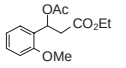
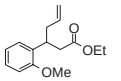
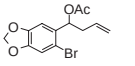
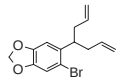
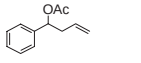
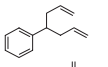
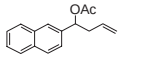
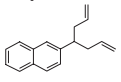
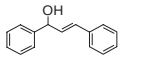
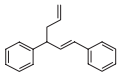
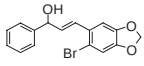
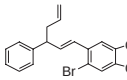
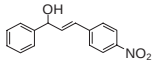
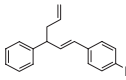
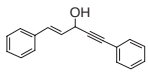
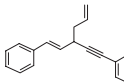
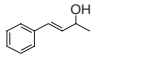
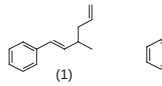
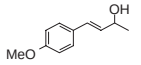
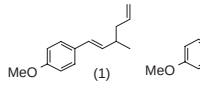
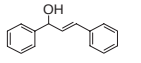
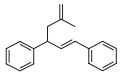
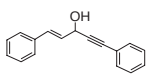
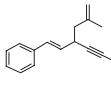


Scheme 1.



Scheme 2.

Table 1. Iodine-catalyzed deoxygenative allylation of benzylic acetates and allylic alcohols

Entry	Substrate	Allyltrimethylsilane	Product[a]	Yield/%[b]	Time/min
A				87	90
B				85	60
C				89	60
D				83	90
E				90	20
F				82	90
G				87	60
H				86	60
I				82	90
J				76	120
K				73	120
L				94	15
M				92	30
N				92	30
O				90	15
P				72 (1) 28 (2)	20
Q				70 (1) 30 (2)	20
R				91	10
S				89	15

[a]All products were characterized by ^{1}H NMR, IR, and mass spectrometry. [b]Isolated yields after purification.

References and Notes

1 Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207; J. A. Marshall, *CHEMTRACTS* **1992**, *5*, 75.

2 E. Colvin, *Silicon in Organic Synthesis*, Butterworth, London, **1981**, p. 97; A. Hosomi, *Acc. Chem. Res.* **1988**, *21*, 200; E. Langkopf, D. Schinzer, *Chem. Rev.* **1995**, *95*, 1375.

3 S. Kobayashi, *Eur. J. Org. Chem.* **1999**, 15.

4 R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, **1985**; C. G. Frost, J. Howarth, J. M. J. Williams, *Tetrahedron: Asymmetry* **1992**, *3*, 1089; B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395.

5 S. A. Godleski, in *Comprehensive Organic Synthesis*, ed. by B. M. Trost, I. Fleming, Pergamon Press, Oxford, **1991**, Vol. 4, p. 585; B. M. Trost, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173; G. J. Dawson, J. M. J. Williams, S. J. Coote, *Tetrahedron: Asymmetry* **1995**, *6*, 2535 and references therein.

6 M. Rubin, V. Gevorgyan, *Org. Lett.* **2001**, *3*, 2705; S. H. Kim, C. Shin, A. N. Pae, H. Y. Koh, M. H. Chang, B. Y. Chung, Y. S. Cho, *Synthesis* **2004**, 1581; G. W. Kabalka, M.-L. Yao, S. Borella, *J. Am. Chem. Soc.*, **2006**, *128*, 11320; G. Kaur, M. Kaushik, S. Trehan, *Tetrahedron Lett.* **1997**, *38*, 2521.

7 H. Togo, S. Iida, *Synlett* **2006**, 2159; X.-F. Lin, S.-L. Cui, Y.-G. Wang, *Tetrahedron Lett.* **2006**, *47*, 4509; W.-Y. Chen, J. Lu, *Synlett* **2005**, 1337; L. Royer, S. K. De, R. A. Gibbs, *Tetrahedron Lett.* **2005**, *46*, 4595; B. K. Banik, M. Fernandez, C. Alvarez, *Tetrahedron Lett.* **2005**, *46*, 2479; S.-Y. Wang, *Synlett* **2004**, 2642; S. Ko, M. N. V. Sastry, C. Lin, C.-F. Yao, *Tetrahedron Lett.* **2005**, *46*, 5771.

8 J. S. Yadav, B. V. S. Reddy, S. R. Hashim, *J. Chem. Soc., Perkin Trans. 1* **2000**, 3082; J. S. Yadav, B. V. S. Reddy, K. Premalatha, T. Swamy, *Tetrahedron Lett.* **2005**, *46*, 2687; J. S. Yadav, B. V. S. Reddy, G. Sabitha, G. S. K. K. Reddy, *Synthesis* **2000**, 1532; J. S. Yadav, B. V. S. Reddy, C. V. Rao, P. K. Chand, A. R. Prasad, *Synlett* **2001**, 1638; J. S. Yadav, B. V. S. Reddy, M. S. Reddy, A. R. Prasad, *Tetrahedron Lett.* **2002**, *43*, 9703; J. S. Yadav, B. V. S. Reddy, K. V. Rao, K. S. Raj, P. P. Rao, A. R. Prasad, D. Gunasekar, *Tetrahedron Lett.* **2004**, *45*, 6505.

9 H. Sakurai, K. Sasaki, A. Hosomi, *Tetrahedron Lett.* **1981**, *22*, 745; M. E. Jung, T. A. Blumenkopf, *Tetrahedron Lett.* **1978**, *19*, 3657.

10 **General procedure**. To a stirred solution of the acetate (1 mmol), and iodine (10 mol %) in dichloromethane (10 mL), allyltrimethylsilane (1.2 mmol) was added slowly dropwise at 0 °C and the mixtures allowed to stir at room temperature for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with water and extracted with dichloromethane (2×10 mL). The combined organic extracts were washed with 15% solution of sodium thiosulfate, followed by water, brine and dried over anhydrous Na_2SO_4. Removal of solvent followed by purification on silica gel using mixtures of ethyl acetate:*n*-hexane (1:9) as eluent afforded pure allyl derivative. **Spectral data for selected products**: Compound **3c**: Colorless solid, m.p. 104–106 °C, IR (KBr): ν 3293, 3188, 4122, 2963, 2917, 1666, 1608, 1550, 1409, 1320, 1267, 995, 911, 832, 754, 546 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (brs, 1H), 7.37 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 2H), 5.72–5.58 (m, 1H), 4.93 (dd, $J = 3.7$, 11.3 Hz, 2H), 2.74 (m, 1H), 2.38–2.14 (m, 2H), 2.13 (s, 3H), 1.22 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ 168.6, 143.0, 136.9, 136.0, 127.3, 120.1, 116.0, 42.7, 39.1, 24.2, 21.5; LCMS: m/z: ($M^+ + Na$): 226; HRMS calcd. for $C_{13}H_{17}NONa$: 226.1207. Found: 226.1206. Compound **3e**: Colorless liquid, IR (KBr): ν 3063, 3026, 2977, 2924, 1640, 1492, 1437, 1216, 1074, 994, 913, 751, 698, 648, 580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.10 (m, 10H), 5.78–5.61 (m, 1H), 5.03–4.89 (m, 2H), 3.96 (t, $J = 7.5$ Hz, 1H), 2.79 (dt, $J = 1.5$, 6.8 Hz, 2H); ^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ 144.6, 136.8, 128.3, 127.9, 126.1, 116.1, 51.2, 39.9; LCMS: m/z: (M^+): 208; HRMS calcd. for $C_{16}H_{16}$: 208.1252. Found: 208.1249. Compound **3l**: Colorless liquid, IR (KBr): ν 3060, 3026, 2975, 2921, 2852, 1640, 1599, 1492, 1447, 1072, 964, 912, 743, 695, 534 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.37–7.07 (m, 10H), 6.36–6.30 (m, 2H), 5.84–5.61 (m, 1H), 5.09–4.91 (m, 2H), 3.55–3.42 (m, 1H), 2.56 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ 143.8, 137.4, 136.4, 133.4, 129.7, 128.4, 127.7, 127.0, 126.3, 126.1, 116.3, 48.9, 40.1; LCMS: m/z: ($M^+ + H$): 235.

Published on the web (Advance View) November 21, 2007; doi:10.1246/cl.2007.1500