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Efficient synthesis of homoallylic alcohols and amines using 2,4,6-trichloro-1,3,5-triazine☆

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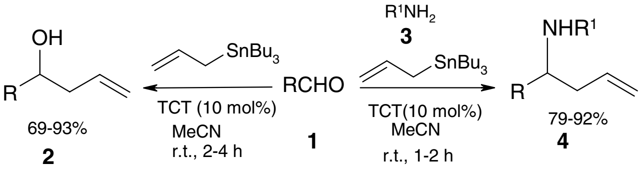
Abstract—The allylation of aldehydes and imines has efficiently been carried out by treatment with allyltributylstannane in the presence of a catalytic amount of 2,4,6-trichloro-1,3,5-triazine at room temperature to form the corresponding homoallylic alcohols and amines, respectively, in high yields.

1. Introduction

Homoallylic alcohols[1] and amines[2] are important building blocks for the construction of various biologically active compounds and hence the syntheses of these compounds are highly useful. Nucleophilic addition of allyltin reagents to carbonyl compounds[3] and imines[4] in the presence of a catalyst is a straightforward method for the synthesis of homoallylic alcohols and amines, respectively. Lewis acids containing boron, aluminum, titanium and tin, which can catalyze this reaction, are extremely moisture sensitive and can cause inconveniences in performing the reaction.

2. Results and discussion

In continuation of our work[5] on the development of useful synthetic methodologies, we report here a facile synthesis of homoallylic alcohols **2** and amines **4** by the allylation of carbonyl compounds and imines (generated in situ from aldehydes and amines) with allyltributylstannane in the presence of a catalytic amount of 2,4,6-trichloro-1,3,5-triazine (TCT, cyanuric chloride) at room temperature (Scheme 1). TCT has recently been utilized in various organic transformations[6] and is a safe and inexpensive reagent. It has been applied here, for the first time, for the preparation of homoallylic alcohols from various aldehydes (Table 1) and of homoallylic amines from different aldehydes and amines (Table 2).



Scheme 1.

The products were formed in good to high yields and no by-products were detected. The yields were found to be better than those reported for several other earlier methods.[3d,e,g,4b] The reaction times required here for the preparation of homoallylic amines (1–2 h) were somewhat shorter than those required for the preparation of homoallylic alcohols (2–4 h). The method is selective for aldehydes only as ketones did not undergo the conversion (Scheme 2).

Both aromatic and aliphatic aldehydes were used for the preparation of homoallylic alcohols and amines. Aromatic aldehydes containing electron-donating as well as electron-withdrawing groups were found to form the products smoothly. A sterically hindered aldehyde such as 2-naphthaldehyde also underwent an easy conversion. The reaction could also be conducted in water (instead of MeCN) as a solvent but the reaction times were longer and the yields were comparatively low.

TCT is known[6d] to react with 'incipient' moisture to form HCl along with 2,4,6-trihydroxy-1,3,5-trazine,

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Keywords: Aldehyde; Imine; Allyltributylstannane; 2,4,6-Trichloro-1,3,5-triazine; Homoallylic alcohol; Homoallylic amine.

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Table 1. Preparation of homoallylic alcohols using TCT[a]

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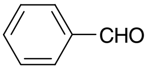
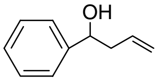
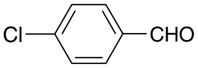
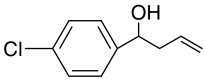
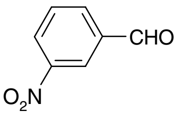
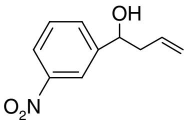
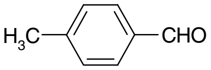
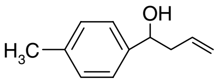
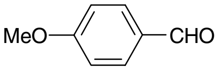
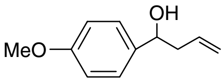
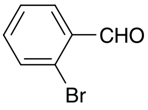
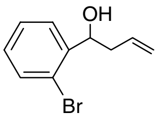
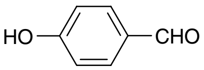
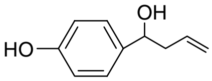
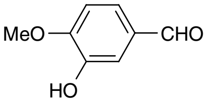
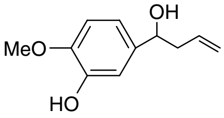
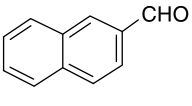
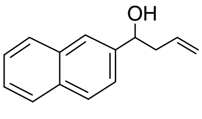
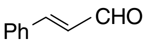
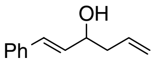
a			2	93
b			2.5	92
c			2	91
d			3	88
e			3.5	79
f			3	92
g			4	69
h			4	71
i			4	78
j			4	85

[a] The structures of the homoallylic alcohols were determined from their spectral (^{1}H NMR and MS) data.

which can activate the carbonyl group or imine system through hydrogen bonding and facilitate the allylation[7] (Scheme 3). The present conversion did not proceed under perfectly anhydrous reaction conditions. An attempt to prepare homoallylic alcohols using aqueous HCl was also unsuccessful.

In conclusion, TCT has efficiently been applied under mild reaction conditions for the allylation of both aldehydes and imines with allyltributylstannane to prepare homoallylic alcohols and amines, respectively, in good to high yields.

3. General procedure for the synthesis of a homoallylic alcohol

To a mixture of aldehyde (1 mmol) and allyltributylstannane (1.2 mmol) in MeCN (5 mL), TCT (10 mol %) was added. The mixture was stirred at room temperature and the reaction was monitored by TLC. After completion, the solvent was evaporated and H_2O (10 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL) and the extract was dried and concentrated. The residue was purified by column chromatography (silica gel, 3% EtOAc in hexane) to afford the pure homoallylic alcohol.

4. General procedure for the synthesis of a homoallylic amine

The homoallylic amine was synthesized following the above procedure using a mixture of aldehyde (1 mmol), amine (1 mmol) and allyltributylstannane (1.2 mmol) in MeCN (5 mL). TCT (10 mol %) was added to the mixture. After completion of the reaction, the

Table 2. Preparation of homoallylic amines using TCT[a]

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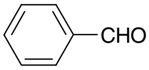
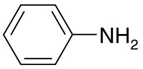
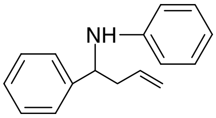
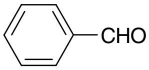
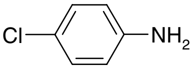
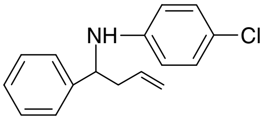
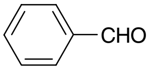
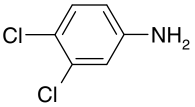
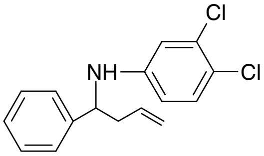
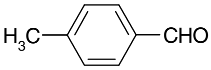
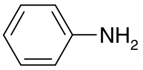
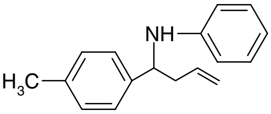
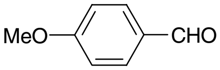
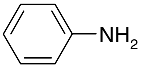
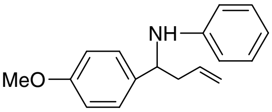
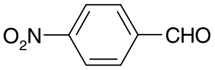
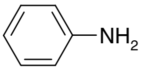
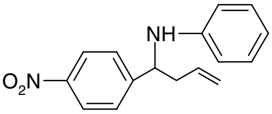
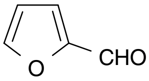
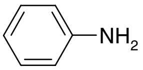
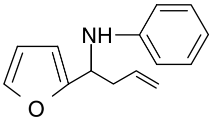
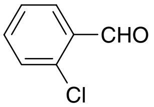
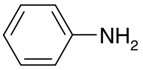
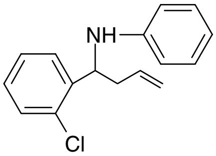
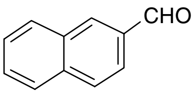
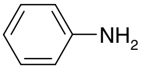
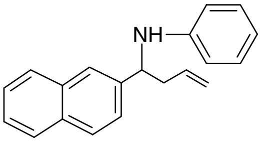
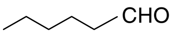
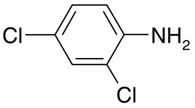
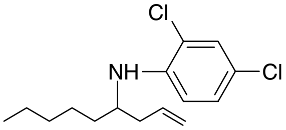
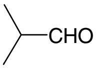
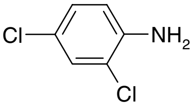
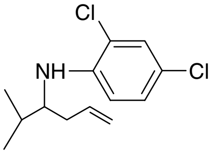
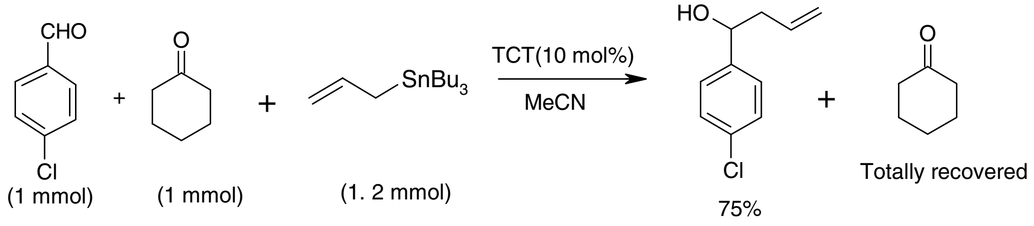
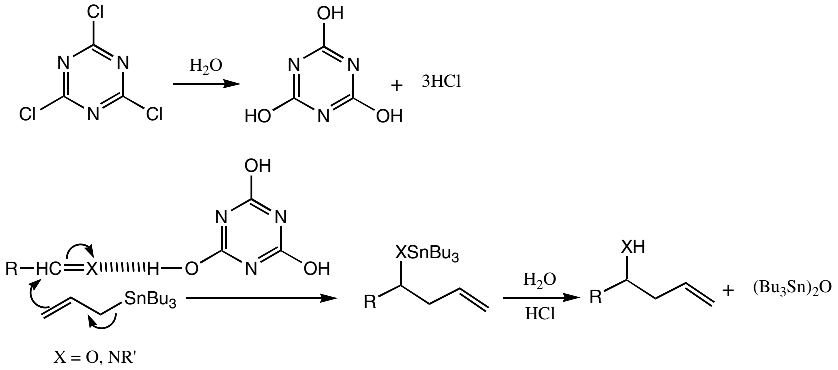
a				1	92
b				2	86
c				2	83
d				1.75	86
e				1.5	84
f				1.25	81
g				2	79
h				1.5	89
i				2	85
j				1.75	89
k				2	81

[a] The structures of the homoallylic amines were settled from their spectral (^{1}H NMR and MS) data.

above work-up procedure was followed. The crude product was purified by column chromatography (silica gel, 1% EtOAc in hexane) to give the pure homoallylic amine.



Scheme 2.



Scheme 3.

Acknowledgements

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References and notes

1. (a) Hoenberer, K. R.; Hamblet, C. L.; Leighton, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 12894; (b) Nicolaou, K. C.; Khim, D. W.; Baati, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3701.
2. (a) Enders, R. D.; Reinhold, U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895; (b) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407.
3. (a) Hamasaki, S.; Chounan, Y.; Horino, H.; Yamamoto, Y. *Tetrahedron Lett.* **2000**, *41*, 9883; (b) Nagayama, S.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2000**, *93*, 567; (c) Kobayashi, S.; Aoyama, N.; Manabe, K. *Synlett* **2002**, 483; (d) Aspinall, H. C.; Bissett, J. S.; Greeves, N.; Levin, D. *Tetrahedron Lett.* **2002**, *43*, 319; (e) Andrade, C. K. Z.; Azevedo, N. R.; Oliveira, G. R. *Synthesis* **2002**, 928; (f) Vartoli, G.; Bosco, M.; Giuliani, A.; Marcantoni, E.; Palmieri, A.; Petrini, N.; Sambri, L. *J. Org. Chem.* **2004**, *69*, 1290; (g) Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Tetrahedron Lett.* **2005**, *46*, 787.
4. (a) Akiyama, T.; Iwai, J.; Onuma, Y.; Kagoshima, H. *J. Chem. Soc., Chem. Commun.* **1999**, *2191*; (b) Aspinall, H. C.; Bissett, J. S.; Greeves, N.; Levin, D. *Tetrahedron Lett.* **2002**, *43*, 323; (c) Akiyama, T.; Onuma, Y. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1157; (d) Yadav, J. S.; Reddy, B. V. S.; Raju, A. K. *Synthesis* **2003**, 883.
5. (a) Das, B.; Ramu, R.; Ravikanth, B.; Reddy, K. R. *Tetrahedron Lett.* **2006**, *47*, 779; (b) Das, B.; Thirupathi, P.; Reddy, V. S.; Rao, Y. K. *J. Mol. Catal. A: Chem.* **2006**, *247*, 233; (c) Das, B.; Krishnaiah, M.; Venkateswarlu, K. *Tetrahedron Lett.* **2006**, *47*, 4457; (d) Das, B.; Ravikanth, B.; Thirupathi, P.; Rao, B. V. *Tetrahedron Lett.* **2006**, *47*, 5041.
6. (a) Falchi, A.; Giacomelli, G.; Porcheddu, A.; Taddei, M. *Synlett* **2000**, 275; (b) Bandgar, B. P.; Pandit, S. S. *Tetrahedron Lett* **2002**, *43*, 3413; (c) Karimi, B.; Hazarkhani, H. *Synthesis* **2003**, 2547; (d) Sharma, G. V. M.; Reddy, K. L.; Lakshmi, P. S.; Krishna, P. R. *Synthesis* **2006**, 55.
7. Krishnaveni, N. S.; Surendra, K.; Kumar, V. P.; Srinivas, B.; Reddy, C. S.; Rao, K. R. *Tetrahedron Lett.* **2005**, *46*, 4299.