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A Simple Two Steps Synthesis of Diallylation From Aldehyde

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Abstract: A new synthesis method of diallyl alkyl carbinols from the reaction of aldehydes with allyl bromide, was prepared by using tin as catalyst, and jone's reagent as Bridge to synthesis diallyl alkyl carbinols in just two steps and a very simple method.

Key words: diallyl alkyl carbinols, jone′s reagent, allyl promide.

1. Introduction

Diallyl alkyl carbinols are intermediates with large synthetic potentials because they can be used to synthesize various compounds[1], such as hydroxyl lactone,[2] polyacrylamide gel,[3] and some natural products.[4] They are usually prepared by the ester reaction with allyl organometallic (e.g. Mg, Zn, Sn, Sm, etc.) reagent or allyl boranes.[7] Usually, this method is used to obtain homoallylic alcohol, but the diallylation of carbonyl compounds is less noticed[5] On the other hand, the selective lntroduction of two alkyl groups at the α-position is rather difficult. This can be done by regloselective consecutive dialkylation. However, the regioselective generation of an anion at the same carbon after the first alkylatlon is difficult[6].

Herein we reported the diallylation of aldehyde promoted by tin metal, which affords in two steps the corresponding diallyl alkyl carbinols in good yields. In (2002) Yu Jia and his co-worker they report that the diallylation of ester they use Dysprosium metalas lanthanides whchich gave us attention paid to the utilization of lanthanides inorganic synthesis Scheme1.[7] Y. Zhang *et al*[8] they reported the diallylation of acyl azides mediated by allylsamarium bromide to to provide the corresponding diallyl alkyl carbinols, Ching-Fa Yao and his co-worker (2007) conversion of various carboxylic acid derivatives into the

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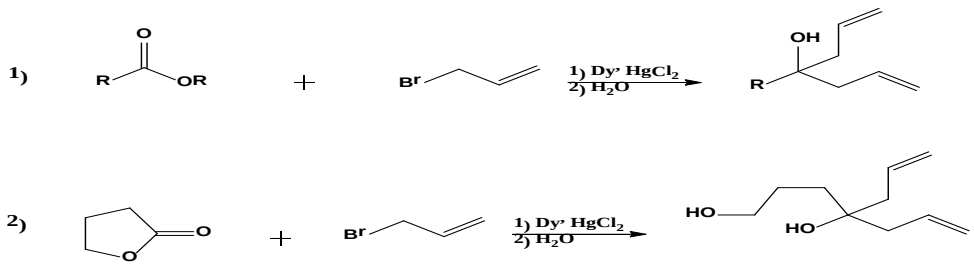
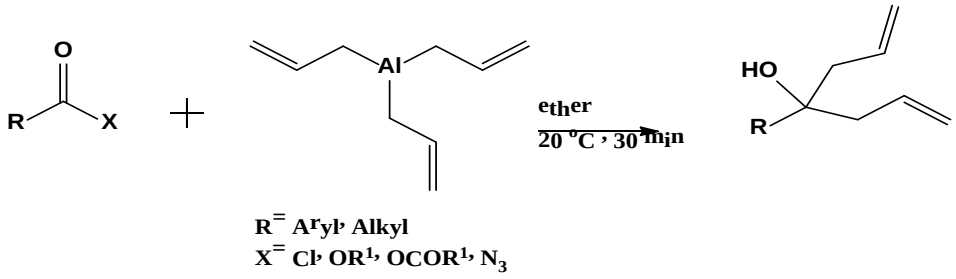
corresponding gem-diallylated compound under mild reaction condition[9],with The use of triallylaluminum mediated Grignard-type addition of carboxylic acid derivative Scheme (2).[9] Some of material use in this method it suffered for the expensive and toxisity, but in the new method, we used simple, available and a low toxicity metrial.

Scheme1: (2002) Yu Jia



Scheme 2: Ching-Fa Yao and his co-worker (2007)



2. Results and Discussion

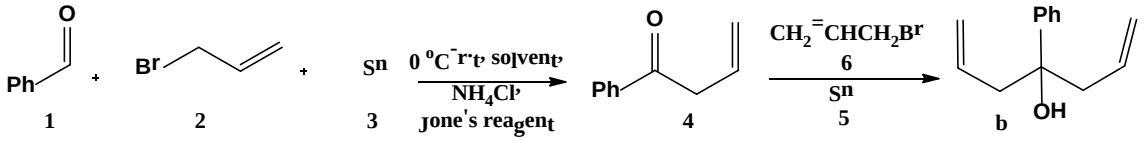
Scheme 3

We initially tested the feasibility of diallylation of aldehyde **1** with H_2C=$CHCH_2Br$ **2** in the presence of Sn **3**, and Jones reagent **4** in THF under air atmosphere. After brief optimization of mole ratio of the reactants, we found that the mole ratio of 1/2/2/(2-4) for aldehyde/ H_2C=$CHCH_2Br$ / Sn /Jones reagent seemed the best ratio to give the product **b** in trace yield, finally used optimization of other reaction conditions.

Due to their high efficiency and the high reactivtiy of grignard reagent to produce RSnBr which guide to react with aldehyde insitu in the presence of jone's reagent to pruduce in two steps the diallyl alkyl carbinols in mild reaction, with the increase of ratio of the allyl bromide and the mitalic tin the yelid% increased (Table 1, entries 1−5). When Et_2O was used in the reaction as solvent, the yeild% in trace (Table 1, entries 7). By using a mix of THF and Et_2O in the reaction together as asolvent , the yeild was increased

and the time of reaction was dicreased (table 1, entries 8), Encouraged by this result, the amount of allyl bromide and the mitalic tin was increased to 4/3 equiv gradually., and the yield of **b** reached to 95% (Table 1, entry 5). Regrettably, the yield of **b** wasn't elevated again when the amount of allyl bromide and the mitalic tin was further increased (Table 1, entry 6) Absence of jone's reaction also examined in the reaction, but the yield of the product was not improved.

Table 1: Optimization of Other Reaction Conditions.[a]



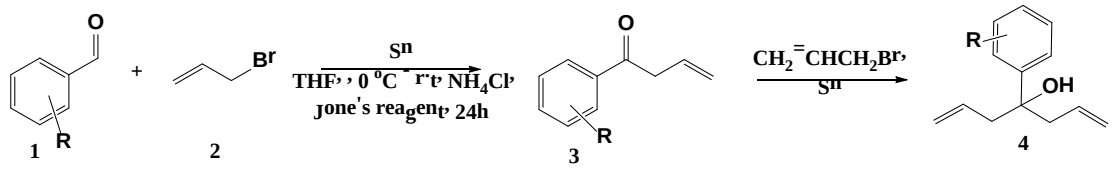
1 2 3 4 5 b

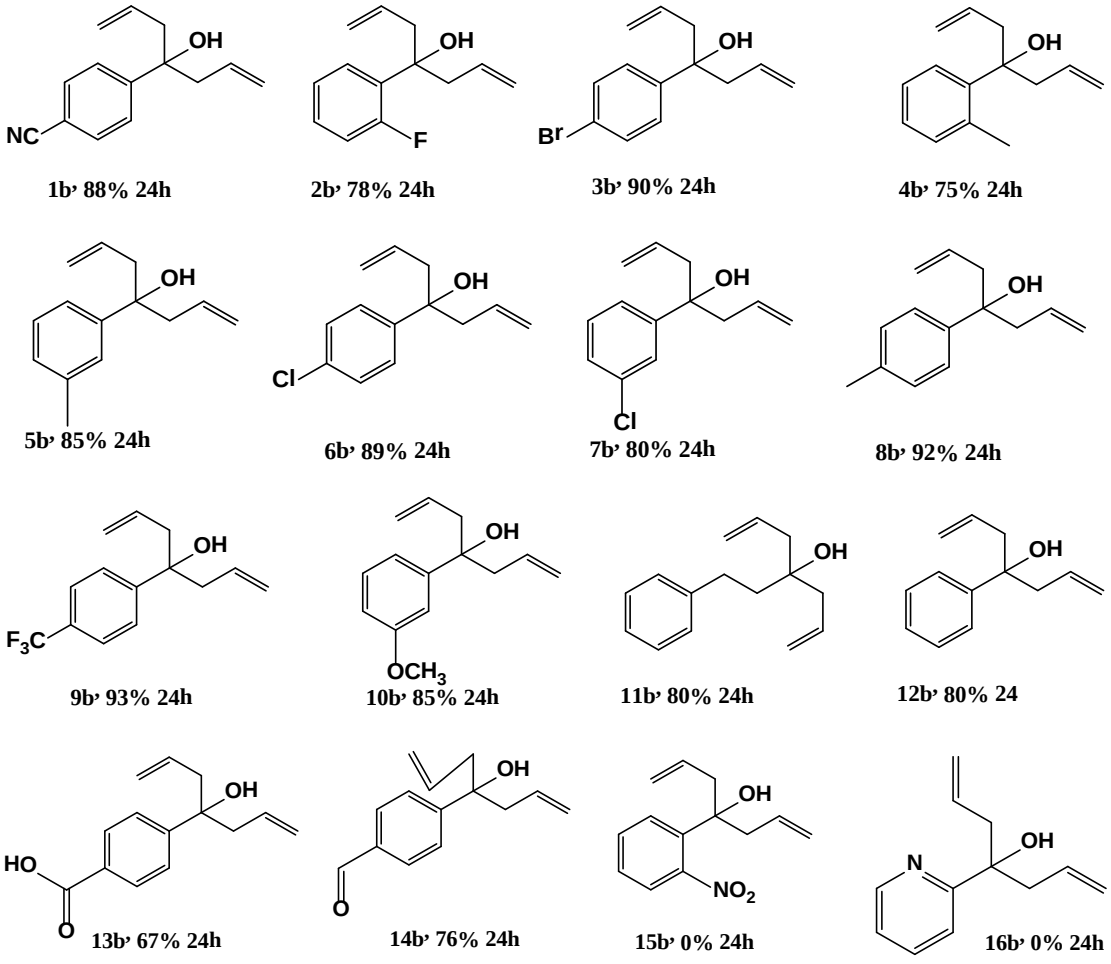
Entry	Mole ratio of 1/2/3	solvent	Time	Yield[b]/%(**b**)
1	1:2:2	THF	12 h	trace
2	1:2.5:2	THF	10 h	20
3	1:2.5:2.5	THF	10 h	51
4	1:3:3	THF	8 h	62
5	1:4:3	THF	6 h	95
6	1:5:4	THF	6 h	80
7	1:3:3	Et_2O	15 min	trace
8	1:3:3	THF/Et_2O	6 h	40

[a] All reactions were carried out by using 1 (0.2 mmol), Jones reagent (0.4-0.8 mmol), r.t.

With the optimal reaction conditions in hand, we next explored the scope of the diallylation with a variety of aldehyde. As shown in Table 2,

Table 2: Substrate Scope of Reaction.[a]





[a] All reactions were carried out by using 1 (2 mmol), 2 (8 mmol), Sn (6 mmol), Jones reagent (4-8 mmol), solvent (4 mL), r.t. [b] Determined by ^{1}H NMR, ^{13}C NMR.

The substrates with various electron-donating or electron-withdrawing groups at the phenyl ring participated in the reaction very well to afford the desired diallayl alkyl carbinols **1b-15b** in high yields (67-95%). The results clearly show that a substituent on the phenyl ring, whether electron-donating or electron-withdrawing, had almost no influence on the reactions. Further, the position of the substituent on the phenyl ring does not affect the product yields. For example, **3b** and **5b** afforded allylated products in excellent yields. Similarly, the use of the corresponding **9b, 12b** and **4b** also resulted in excellent yields.

Sterically acid anhydrides such as **13b** (entry 18) and **15b** also afforded good yields of products but unfortionatly **16b** not give any result.

3. Experimental

The metallic tin used in the reactions was prepared from a tin reacting with HCl10%. THF was treated with sodium and distilled before use. Ethyl acetate and petroleum ether used in the flash column chromatography were distilled before use. Reaction of aldehyde with Allyl Bromide and Metallic tin in a simple two steps synthesis of diallylation from aldehyde.

A mixture of aldehyde (2 mmol), allyl bromide (8 mmol), tin powder (6mmol) and anhydrous THF (8 mL) was stirred at 0^{o} C for 30 min and then add jone's reagent (2-4 mmol) , the mixture were stirred at room temperature for 6 h. Then the reaction mixture was treated with 10 mL of saturated aqueous NH_4Cl and extracted with ethyl acetate. next step to ad allyl bromide (8mmol), tin powder (6mmol) in same flask and then extracted with ethyl acetate. The combined organic extracts were dried over Sodium sulfate. After the evaporation of ethyl acetacte , the residue was purified by flash column chromatography, a mixture of petroleum ether and ethyl acetate being used as the elution solvent, and from which the products were isolated.

4. Conclusion

In conclusion, we report on the development of a simple two steps synthesis of diallylation and general procedure for the diallyl alkyl carbinols of derivatives of aldehyde using tin , jone's reagent and allyl promide . The advantages of the reaction are as follows: (1) the reaction is applicable to a wide variety of aldehyde derivatives, (2) the preparation of jone's reagent and allyltin promide is relatively straightforward, (3) the reaction time is short, (4) the reaction proceeds at room temperature, (5) the product yields are high and (6) the reaction proceeds, even when sterically hindered starting products are employed. To the best of our knowledge, this is the first report of the use jone's reagent as akey for the diallyl alkyl carbinols of aldehyde. Because of the advantages listed above, the preparation of diallyl alkyl carbinols using jone's reagent and allylbromide and tin in a simple two steps makes this method an attractive alternative to existing processes.

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References

[1]. Y. Jia, M. Zhang, F.Tao, J. Zhou, Allylation Of Esters Promoted By Metallic Dysprosium In The Presence Of Mercuric Chloride, *Syn. Comm*., 2002, 32 (18) 2829-2835

[2]. E. Bardshiri, T.J. Simpson, Studies on a Synthesis of (RS)-Mevalonic Acid Lactone, *J. Chem. Soc. Perkin Trans*., 1984, 1 (8) 1765-1767.

[3]. D.F. Hochstrasser, A. Patchornik, C.R Merril, Development of polyacrylamide gels that improve the separation of proteins and their detection by silver staining. *Anal. Biochem.*, 1988, 173**,** 412-423.

[4]. D.Y. Kong, H.T. Li, S.Q. Luo, X.H. Lei, Studies on the chemical components of Viscum coloratum. VI. Chirality of the acyl group of viscumneoside IV, *Acta pharmaceutica Sinica*., 1990, 25 (5), 349-52.

[5]. J. Li, Y. Liu, Y. Zhang, Gem-diallylation of acyl azides with allylsamarium bromide under mild conditions, *J. Chem. Research (S).*, 2003, 438-439.

[6]. I. Shimizu, Y. Ohashi, J. Tsuji, A new One-pot Method For α, α-allylation Of Ketones based On The Palladium-Catalyzed Reaction Of Allylic Cabronates And allyl β-Keto Carbooxylates Under Neutral Conditions, *Tetrahedron Letters*., 1983, 24 (36) 3865-3868.

[7]. Yu Jia, Mingfu Zhang, Fenggang Tao & Jingyao Zhou *Synthetic Communications* 32: 18 (2002) 2829–2835.

[8]. X. Fan, Y. Zhang, Preparation of dihomoallylic secondary amines through Samarium mediated allylation of oximes. *Tetrahedron Letters.*, 2002, 43, 5475-5478.

[9]. K.-H. Shen, C.-W. Kuo, C.-F. Yao, *Tetrahedron Letters* 48 (2007) 6348-6351