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

Barbier-Type Allylation of Aldehydes and Ketones with Metallic Lead in Aqueous Media

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Published online: 22 Aug 2006.

SYNTHETIC COMMUNICATIONS, 27(11), 1899-1906 (1997)

BARBIER-TYPE ALLYLATION OF ALDEHYDES AND KETONES WITH METALLIC LEAD IN AQUEOUS MEDIA

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Abstract: Homoallylic alcohols can be obtained from allylation of aldehydes and ketones with allyl bromide promoted by metallic lead. These reactions can be carried out smoothly in aqueous media.

Barbier-type allylation of carbonyl compounds with in situ generated allyl metal reagents furnish important tactics for making carbon-carbon linkages in organic synthesis.[1] We recently reported the reactions of aldehydes and ketones with halides promoted by tin.[2] These reactions can be carried out in aqueous media and the reaction conditions were quite mild. Furthermore, the tedious task of protection-deprotection of certain functional groups can be avoided. In a consequent extension of this work, we have now found that the allylation of

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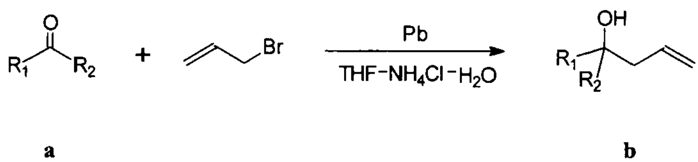
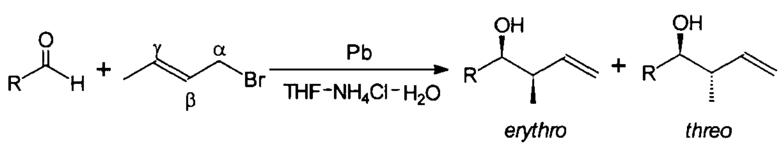
aldehydes or ketones with allyl bromide was successfully performed with metallic lead in aqueous media. These reactions gave homoallylic alcohols as the products.

The lead-promoted allylation reactions can be successfully applied to various aldehydes and ketones (**Scheme 1**), and some results are shown in **Table 1**. Allylations of aromatic aldehydes (entry 1-6) proceed smoothly to give homoallylic alcohols in excellent yields, while lower yields were obtained when aliphatic aldehydes and ketones (Entry 7-11) were used as the reactants. Only 1,2-addition products were obtained when α,β-unsaturated aldehydes (Entry 6, 9) were used. The reactions proceeded smoothly with substrates containing reactive groups such as halogen or hydroxyl (Entry 2, 5).



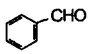
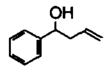
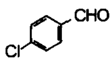
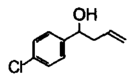
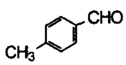
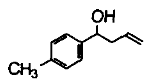
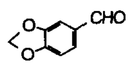
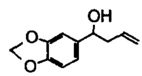
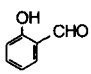
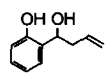
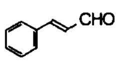
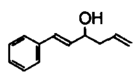
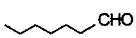
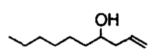
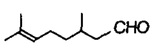
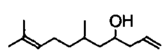
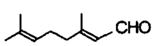
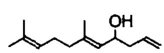
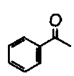
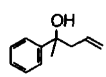
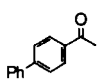
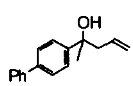
Scheme 1

As shown in **Scheme 2**, the reactions of aldehydes and crotyl bromide with metallic lead only gave γ-adduct products. Furthermore, medium *erythro*-selectivity was obtained in these reactions. (**Table 2**)



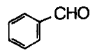
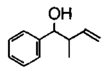
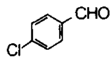
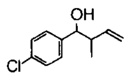
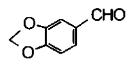
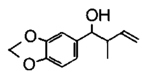
Scheme 2

Table 1

Entry	Carbonyl compounds (a)		Products (b)		Yield [a] (%)
1		**1a**		**1b**	99
2		**2a**		**2b**	99
3		**3a**		**3b**	96
4		**4a**		**4b**	99
5		**5a**		**5b**	98
6		**6a**		**6b**	98
7		**7a**		**7b**	18
8		**8a**		**8b**	26
9		**9a**		**9b**	52
10		**10a**		**10b**	20
11		**11a**		**11b**	15

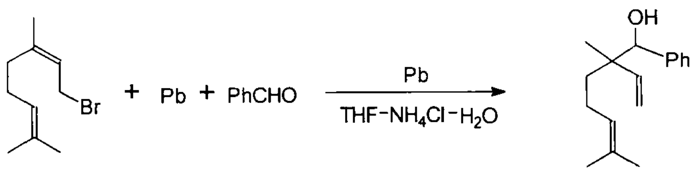
[a] Isolated yields

Table 2

Entry	Aldehydes		Products		Yield [a] (%)	*erythro* : *threo* [b]
12		**12a**		**12b**	94	75 : 25
13		**13a**		**13b**	99	81 : 19
14		**14a**		**14b**	99	79 : 21

[a] Isolated yields.
[b] Product ratios determined by ^{1}H NMR.

Most of the linalyl containing compounds are natural occurring and biological active species. They are used in fragrance and pharmaceutical industry. Here we have studied the reaction of geranyl bromide and benzaldehyde in the presence of metallic lead (**Scheme 3**). This reaction took place smoothly and linalyl carbinol (15b) was obtained by one pot reaction with good yield. We hope this methodology will be a promising tool for the synthesis of natural compounds.



15a **15b**

Scheme 3

General experimental procedure:

A suspension of 1 mmol of aldehyde or ketone (**a**), 2.5 mmol of allyl bromide, 4 mmol of lead powder, THF (5 mL), and saturated aqueous solution of ammonium chloride (3 mL) was stirred at room temperature for 20 h. Then extracted with ether (20 mL × 3), the combined extracts were dried over anhydrous sodium sulfate. The ether was removed and the residue was purified by column chromatography to give **b**.

1b[3]: ν_{max}: 3350 (s, O-H), 1640 (m, C=C), 910 (m, C=CH_2) cm^{-1};

δ_H (CCl_4, TMS): 2.30 (t, 2H), 2.55 (s, 1H, OH), 4.45 (t, 1H), 4.80-5.90 (m, 3H), 7.15 (s, 5H) ppm.

2b[3]: ν_{max}: 3350 (s, O-H), 1640 (m, C=C), 910 (m, C=CH_2) cm^{-1};

δ_H (CCl_4, TMS): 2.03 (s, 1H, OH), 2.33 (t, 2H), 4.45 (t, 1H), 4.80-5.90 (m, 3H), 7.15 (s, 4H) ppm.

3b[4]: ν_{max}: 3350 (s, O-H), 1635 (m, C=C), 910 (m, C=CH_2) cm^{-1};

δ_H (CCl_4, TMS): 1.80 (s, 1H, OH), 2.00-2.47 (m, 5H), 4.40 (t, 1H), 4.60-5.90 (m, 3H), 7.00 (s, 4H) ppm.

4b[3]: ν_{max}: 3350 (s, O-H), 1630 (m, C=C), 910 (m, C=CH_2) cm^{-1};

δ_H (CCl_4, TMS): 2.30 (t, 2H), 2.60 (s, 1H, OH), 4.50 (t, 1H), 4.90-5.80 (m, 3H), 5.90 (s, 2H), 6.70 (d, 3H) ppm.

5b[6b]: ν_{max}: 3300 (s, O-H), 1630 (m, C=C), 910 (m, C=CH_2) cm^{-1};

δ_H (CCl_4, TMS): 2.50 (t, 2H), 4.67 (t, 1H), 4.77-5.90 (m, 5H), 6.30-7.00 (m, 4H) ppm.

6b[3]: ν_{max}: 3400 (s, O-H), 1640 (m, C=C), 910 (m, C=CH_2) cm^{-1};

δ_H (CCl_4, TMS): 2.23 (t, 2H), 3.00-3.30 (br, 1H, OH), 3.93-4.27 (m, 1H), 4.67-6.60 (m, 5H), 7.07 (s, 5H) ppm.

7b[4]**:** ν_{max}: 3350 (s, O-H), 1635 (m, C=C), 905 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 0.73-1.50 (m, 14H), 1.83-2.10 (m, 2H), 3.27-3.50 (m, 1H), 4.60-6.00 (m, 3H) ppm.

8b[7]**:** ν_{max}: 3350 (s, O-H), 1635 (m, C=C), 905 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 1.53-1.90 (m, 9H), 1.87-2.30 (m, 9H), 2.47 (s, 1H, OH), 4.13 (q, 1H), 4.73-5.87 (m, 4H) ppm.

9b[7]**:** ν_{max}: 3350 (s, O-H), 1635 (m, C=C), 905 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 1.40 (s, 1H, OH), 1.50-1.87 (m, 9H), 1.87-2.30 (m, 6H), 4.17 (q, 1H), 4.70-5.90 (m, 5H) ppm.

10b[5]**:** ν_{max}: 3450 (s, O-H), 1630 (w, C=C), 910 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 1.30 (s, 3H), 1.90 (s, 1H, OH), 2.10-2.45 (m, 2H), 4.70-5.60 (m, 3H), 6.90-7.27 (m, 5H) ppm.

11b: ν_{max}: 3450 (s, O-H), 1630 (w, C=C), 910 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 1.43 (s, 3H), 1.67-1.97 (br, 1H, OH), 2.30-2.60 (m, 2H), 4.67-5.70 (m, 3H), 7.00-7.50 (m, 9H) ppm.

12b[6a]**:** ν_{max}: 3350 (s, O-H), 1630 (w, C=C), 905 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 0.70-1.03 (m, 3H), 2.10-2.47 (m, 2H), 4.08 (d, J=7.5Hz, 0.25H, *threo*), 4.24 (d, J=6.0Hz, 0.75H, *erythro*), 4.63-5.73 (m, 3H), 7.03 (s, 5H) ppm.

13b[6b]**:** ν_{max}: 3400 (s, O-H), 1635 (m, C=C), 910 (s, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 0.70-1.07 (m, 3H), 2.00 (s, 1H, OH), 2.33 (q, 1H), 4.13 (d, J=7.0Hz, 0.19H, *threo*), 4.30 (d, J=5.5Hz, 0.81H, *erythro*), 4.60-6.00 (m, 3H), 7.03 (s, 4H) ppm.

14b: ν_{max}: 3350 (s, O-H), 1630 (w, C=C), 905 (m, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 0.77-1.00 (m, 3H), 2.03-2.50 (m, 2H), 4.17 (d, J=7.5Hz, 0.21H, *threo*), 4.33 (d, J=6.0Hz, 0.79H, *erythro*), 4.77-5.80 (m, 3H), 5.90 (s, 2H), 6.60-6.80 (m, 3H) ppm.

15b[8]: ν_{max}: 3450 (s, OH), 1640 (w, C=C), 910 (s, $C=CH_2$) cm^{-1};

δ_H (CCl_4, TMS): 0.79 (s, 3H), 1.10-2.00 (m, 11H), 4.16-47 (m, 1H), 4.79-6.00 (m, 4H), 6.56-6.66 (m, 5H) ppm.

Acknowledgments:

We acknowledge the National Natural Science Foundation of China and the Foundation of National Key Laboratory of Bioorganic and Natural Product Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica for financial support.

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(Received in the UK 28th October 1996)