Efficient allylation of carbonyl compounds with allyl chlorides in water

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Dedicated to Professor Chengye Yuan on the occasion of his 80th birthday

(received 25 Feb 04; accepted 22 June 04; published on the web 23 June 04)

Abstract

A novel mediation system, Zn-$InCl_3$ (cat.)/NH_4Cl was employed in the Barbier–type allylation. As a result, the allylation with allyl chloride in water took place smoothly under mild conditions. Various aldehydes and even ketones could be employed to afford the corresponding alcohols in high yields. The stereochemistry of the allylation reactions was also briefly discussed.

Keywords: Allylation, allyl chloride, carbonyl compounds, homoallylic alcohol

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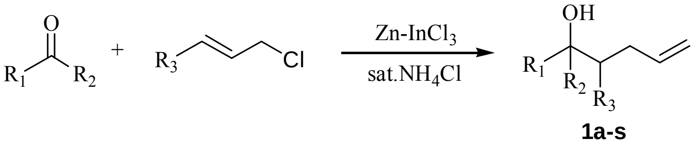
Introduction

Recently, organic reactions in aqueous media have attracted more and more attention in organic synthesis because of their environmental benefits and the favorable effects of water on organic transformations.[1] Among the reactions in aqueous media, allylations of carbonyl compounds with allylic organometallic compounds or allyl halides are of particular interest because they are the convenient method to form C-C bond and to generate homoallylic alcohols, which are important building blocks in natural product synthesis.[2] Many metals such as Mg,[3] Zn,[4] Sn,[5] In,[6] Bi[7] have been employed as the mediators to promote the allylation under mild conditions. In these reactions, the allyl halides used were generally allyl bromides. Allyl chlorides, which are cheaper and more stable than allyl bromidse, are hardly effective.[8] Therefore, it is important to develop the allylation methods with allyl chlorides under mild conditions. Herein we report a new and facile allylation method with allyl chloride in water (Scheme 1).



Scheme 1

Results and Discussion

Zinc metal has been demonstrated to be the popular and facile mediator to promote the allylation reactions.[4] Initially, we attempted to carry out the allylation of allyl chloride with benzaldehyde under the mediation of zinc powder. However, only a trace amount of the desired product was obtained when the reaction was performed in neat water even if allyl chloride was replaced with allyl bromide. It was assumed that there was a water-insoluble oxide film on the surface of zinc metal, which resulted in the loss of the reactivity of mediator zinc and the failure of the allylation. Thus, we tested different acids such as HCl, HBr, HOAc and NH_4Cl to erase this oxide film. Finally we found that saturated NH_4Cl aqueous solution was the best clean agent for this film. Thus, saturated NH_4Cl aqueous solution was applied in the above reaction. As a result, the yield of the allylation product increased to 30%.

Considering that Lewis acids were usually employed as auxiliary agents to promote the allylation,[9] different Lewis acids such as $SnCl_2$, $SnCl_4$, $BiCl_3$ and $InCl_3$ were tested to improve the above allylation and the results are summarized in Table 1. As can be seen in Table 1, all the Lewis acids screened promote, more or less, the allylation (entries 2 - 5, Table 1). Among them, indium trichloride was the most effective one. With the employment of indium trichloride, the reaction rate was accelerated significantly and the product yield was improved dramatically (entry 5, Table 1). The amount of indium trichloride used had a large influence on the allylation outcome. With 5 mol% of indium trichloride, the product yield was improved from 30% to 52% (entries 1 and 6, Table 1). When the amount of $InCl_3$ was increased to 10 mol%, the yield was further improved (entry 7, Table 1). However, when the amount of $InCl_3$ was over 20%, the product yield decreased gradually (entries 8 and 9, Table 1). Such results should be compared to the previously reported allylation of allyl bromide with benzaldehyde, which was conducted in THF-H_2O (5:2) and argon atmosphere for 50h.[10]

Table 1. Zn-Lewis acid mediated allylation of benzaldehyde[a]

Entry	Lewis acid (mol%)	Time (h)	Yield[b](%)
1	_	24	30
2	$SnCl_4$ (20%)	12	39
3	$BiCl_3$ (20%)	12	31
4	$SnCl_2$ (20%)	12	56
5	$InCl_3$ (20%)	6	90 (85)[c]
6	$InCl_3$ (5%)	12	52
7	$InCl_3$ (10%)	6	92 (88)[c]
8	$InCl_3$ (50%)	12	80
9	$InCl_3$ (100%)	12	73

[a] Reaction conditions: PhCHO (1 mmol), allyl chloride (1.5 mmol), zinc powder (2 mmol) and a Lewis acid in sat. NH_4Cl (4 ml) at r.t. for a specified time. [b] Estimated by HPLC. [c] Isolated yield.

A variety of carbonyl compounds were then allylated under the above optimized condition and the results are summarized in Table 2. Both aldehydes and ketones were converted smoothly to the corresponding homoallylic alcohols in good to excellent yields. No pinacol coupling products or reduced products were observed. The results showed that the substituents on phenyl ring, whether electron-donating or electron-withdrawing, had almost no influence on the allylations (entries 1-6, Table 2). Moreover, the allylation with crotyl chloride gave the corresponding adducts in excellent yields regardless of whether the substrate is an aldehyde or a ketone (entries 15-19, Table 2). To the best of our knowledge, no report on the corresponding allylation of ketone with crotyl chloride in water was found. Only a few examples with allyl bromide were reported, in which the corresponding allylations hardly took place or gave the corresponding adducts in low yields and the reactions took long time.[11] It is interesting to note that the substrates with a hydroxyl group such as 2-hydroxylbenzaldehyde, 2-hydroxyl-5-methoxybenzaldehyde and 3-hydroxybuta-2-one gave slightly higher yields probably because of their better solubility in water (entries 8, 9, 14, Table 2).

With crotyl chloride, the reactions were highly regioselective (entries 15-19, Table 2). The allylation gave the corresponding γ adducts exclusively except for benzaldehyde, in which the ratio of γ to α adduct was around 33 : 1. In all the cases, syn-isomers were favored over the anti-isomers. These results are different from those reported in the literature in which no stereoselectivity was observed[12] or the anti-isomers were favored.[13] The reason for the differences in the stereoselectivities is still unclear.

Table 2. Alllylation of carbonyl compounds with allyl chlorides in sat. NH_4Cl

Entry	R_1	R_2	R_3	Product	Yield [a](%)/time (h)
1	Ph	H	H	**1a**	88/6(85/2.5)[b]
2	4-$CH_3OC_6H_4$	H	H	**1b**	89/8
3	4-ClC_6H_4	H	H	**1c**	82/8
4	piperonyl	H	H	**1d**	88/8
5	1-naphthyl	H	H	**1e**	80/8
6	4-$CH_3C_6H_4$	H	H	**1f**	85/8
7	2-furyl	H	H	**1g**	92/7
8	2-OHC_6H_4	H	H	**1h**	96/3(94/2)[b]
9	2-OH-5-$CH_3OC_6H_3$	H	H	**1i**	94/4
10	n-C_6H_{13}	H	H	**1j**	78/10(81/6)[b]
11	Ph	Me	H	**1k**	85/12(83/5)[b]
12	Ph	Ph	H	**1l**	58/15(54/6)[b]
13	c-$(CH_2)_5$		H	**1m**	75/12(76/7)[b]
14	$CH_3CH(OH)$	Me	H	**1n**	87/5
15	Ph	H	Me	**1o**	95[c]/10 γ:α=33:1

Table 2. Continued

Entry	R_1	R_2	R_3	Product	Yield [a](%)/time (h)
					syn:anti=76:24
16	4-ClC_6H_4	H	Me	**1p**	98/3 syn:anti=71:29
17	4-$CH_3C_6H_4$	H	Me	**1q**	97/4 syn:anti=72:28
18	Ph	Me	Me	**1r**	92/12 syn:anti=72:28
19	4-ClC_6H_4	Me	Me	**1s**	93[d]/10 syn:anti=76:24

[a] Isolated yields. [b] Allyl bromide was used. [c] Combined yields. The ratio was determined by ^1H NMR. [d] The yield was estimated by ^1HNMR.

In conclusion, we have developed a novel mediation system for the allylation of carbonyl compounds with the more popular and less expensive allyl chlorides, giving the corresponding homoallylic alcohols in good to excellent yields. Both aldehydes and ketones can be allylated smoothly. Further investigation on the role of $InCl_3$ is in progress in our laboratory.

Experimental Section

General Procedures. All the chemicals were commercially available and directly used without further purification. IR spectra were performed on a Bruker FT-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were measured on a Brucker-300MHz spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. HRMS data were collected on a Micromass GCT mass spectrometer with an EI mode.

General method for allylation

To a mixture of a carbonyl compound (1 mmol), allyl chloride (1.5 mmol) and indium trichloride (0.1 mmol) in saturated aqueous NH_4Cl solution (4 ml) was added zinc powder (2 mmol) in one potion with stirring. The mixture was vigorously stirred at room temperature for a specified time. The resulting mixture was then extracted with ethyl acetate and the combined organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography over silica gel to give the pure product 1. The corresponding product was identified by ^1H NMR, ^{13}C NMR, IR and HRMS.

1-Phenylbut-3-en-1-ol (1a). IR (film): 3384, 3075, 1640cm^{-1}; ^1H NMR: δ 2.50 (t, J = 7.1, 6.6 Hz, 2H), 2.55-2.65 (br, 1H), 4.72 (dd, J = 7.1, 5.6 Hz, 1H), 5.11-5.18 (m, 2H), 5.74-5.83 (m, 1H), 7.24-7.35 (m, 5H); ^{13}C NMR: δ 43.6, 73.4, 117.9, 125.9, 127.4, 128.3, 134.6, 143.9; HR MS: calc. for $C_{10}H_{10}$ (M^+-H_2O) 130.0783 found 130.0769.

1-(4-Methoxyphenyl)but-3-en-1-ol (1b). IR (film): 3405, 3074, 1640cm^{-1}; ^{1}H NMR: δ 2.41-2.56 (m, 3H), 3.77 (s, 3H), 4.64 (t, J = 6.5 Hz, 1H), 5.08-5.15 (m, 2H), 5.70-5.81 (m, 1H), 6.84-6.86 (dt, J = 8.5 Hz, 2H), 7.25 (dt, J = 8.5 Hz, 2H); ^{13}C NMR: δ 43.6, 76.0, 78.7, 113.7, 117.8, 127.1, 134.8, 136.3, 158.9; HRMS: calc. for $C_{11}H_{12}O$ (M^+-H_2O) 160.0888, found 160.0855.

1-(4-Chlorophenyl)but-3-en-1-ol (1c). IR (film): 3380, 3080, 1640cm^{-1}; ^{1}H NMR: δ 2.43-2.50 (m, 2H), 2.52-2.60 (br, 1H), 4.68-4.72 (dd, J = 5.4, 2.2 Hz, 1H), 5.13-5.18 (m, 2H), 5.70-5.84 (m, 1H), 7.26-7.33 (m, 4H); ^{13}C NMR: δ 43.6, 72.7, 118.4, 127.3, 128.4, 133.0, 134.0, 142.4; HRMS: calc. for $C_{10}H_9Cl$ (M^+-H_2O) 164.0393, found 164.0382.

1-Benzo[1,3]dioxol-5-ylbut-3-en-1-ol (1d). IR (film): 3384, 3075, 1640cm^{-1}; ^{1}H NMR: δ 2.40-2.53 (m, 3H), 4.60 (t, J = 6.5 Hz, 1H), 5.09-5.16 (m, 2H), 5.71-5.81 (m, 1H), 5.92 (s, 2H), 6.73-6.79 (m, 2H), 6.84 (s, 1H); ^{13}C NMR: δ 43.8, 73.4, 101.0, 106.5, 108.1, 118.1, 119.3, 134.6, 138.2, 146.9, 147.7; HRMS: calc. for $C_{11}H_{10}O_2$ (M^+-H_2O) 174.0681, found 174.0665.

1-(Naphthalen-1-yl)but-3-en-1-ol (1e). IR (film): 3380, 3070, 1640cm^{-1}; ^{1}H NMR: δ 2.47-2.70 (m, 3H), 5.09-5.17 (m, 2H), 5.40-5.42 (m, 1H), 5.78-5.91(m, 1H), 7.17-7.99 (m, 7H); ^{13}C NMR: δ 43.1, 70.2, 118.6, 123.1, 123.2, 125.6, 125.7, 126.3, 128.2, 129.2, 130.5, 135.0, 139.6; HRMS: calc. for $C_{14}H_{14}O$ (M^+) 198.1045, found 198.1058.

1-(4-Methylphenyl)but-3-en-1-ol (1f). IR (film): 3382, 3075, 1640cm^{-1}; ^{1}H NMR: δ 2.31 (s, 3H), 2.42-2.46 (m, 3H), 4.60 (t, J = 6.5 Hz, 1H), 5.06-5.12 (m, 2H), 5.70-5.76 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H); ^{13}C NMR: δ 21.2, 43.8, 73.7, 118.2, 125.9, 129.2, 134.8, 137.2, 141.1; HRMS: calc. for $C_{11}H_{12}$ (M^+-H_2O) 144.0939, found 144.0924.

1-Furan-2-ylbut-3-en-1-ol (1g). IR (film): 3377, 3078, 1642cm^{-1}; ^{1}H NMR: δ 1.93-2.12 (br, 1H), 2.61-2.66 (m, 2H), 4.76 (t, J = 6.1 Hz, 1H), 5.14-5.22 (m, 2H), 5.74-5.84 (m, 1H), 6.25 (d, J = 2.6 Hz, 1H), 6.33 (q, J = 2.6, 1.5 Hz, 1H), 7.39(d, J = 1.5 Hz, 1H); ^{13}C NMR: δ 40.3, 67.2, 106.3, 110.4, 118.8, 133.9, 142.2, 156.3. HRMS: calc. for C_8H_8O (M^+-H_2O) 120.0575, found 120.0569.

2-(1-Hydroxybut-3-enyl)-phenol (1h). IR (film): 3335, 1641cm^{-1}; ^{1}H NMR: δ 2.50-2.70 (m, 2H), 3.12-3.40 (br, 1H), 4.72-4.91 (m, 1H), 5.14-5.18 (m, 2H), 5.73-5.87 (m, 1H), 6.82-7.17 (m, 4H), 8.02-8.23 (br, 1H); ^{13}C NMR: δ 42.1, 74.5, 117.2, 119.1, 119.9, 126.7,127.2, 128.9, 134.0, 155.3; HRMS: calc. for $C_{10}H_{11}O$ (M^+-H_2O) 147.0810, found 147.0754.

2-(1-Hydroxybut-3-enyl)-4-methoxyphenol (1i). IR (film): 3362, 2938, 1641cm^{-1}; ^{1}H NMR: δ 2.54-2.57 (m, 2H), 3.70 (s, 3H), 3.72-3.90 (br, 1H), 4.65-4.85 (m, 1H), 5.10-5.16 (m, 2H), 5.70-5.90 (m, 1H), 6.53 (d, J = 2.2 Hz, 1H), 6.65-6.75 (m, 2H), 7.74-7.92 (br, 1H); ^{13}C NMR: δ 41.9, 55.8, 74.0, 112.8, 113.7, 117.4, 118.6, 128.0, 134.1, 148.9, 152.8; HRMS: calc. for $C_{11}H_{14}O_3$ (M^+) 194.0943, found 194.0942.

Dec-1-en-4-ol (1j). IR (film): 3356, 2928, 1641cm^{-1}; ^{1}H NMR: δ 0.86 (t, J = 6.7 Hz, 3H), 1.27-1.44 (m, 10H), 1.70-1.90 (br, 1H), 2.06-2.16 (m, 1H), 2.24-2.32 (m, 1H), 3.60-3.66 (m, 1H), 5.08-5.14 (m, 2H), 5.77-5.86 (m, 1H); ^{13}C NMR: δ 14.0, 22.6, 25.6, 29.3 31.8, 36.8, 41.9, 70.7, 117.7, 134.9; HRMS: calc. for $C_{10}H_{18}$ (M^+-H_2O) 138.1409, found 138.1401.

2-Phenylpent-4-en-2-ol (1k). IR (film): 3418, 3085, 1647cm^{-1}; ^{1}H NMR: δ 1.54 (s, 3H), 1.98-2.17 (br, 1H), 2.45-2.50 (m, 1H), 2.65-2.71 (m, 1H), 5.09-5.15 (m, 2H), 5.55-5.69 (m, 1H), 7.20-7.45 (m, 5H); ^{13}C NMR: δ 30.3, 48.7, 73.8, 119.6, 124.9, 126.8, 128.3, 133.9, 147.8; HRMS: calc. for $C_{11}H_{14}O$ (M^+) 162.0790, found 162.0794.

1,1-Diphenylbut-3-en-1-ol (1l). IR (film): 3564, 3479, 3059, 1638cm^{-1}; ^{1}H NMR: δ 2.42-2.60 (br, 1H), 3.05 (d, J = 7.2 Hz, 1H), 5.14-5.25 (m, 2H), 5.56-5.68 (m, 1H), 7.14-7.44 (m, 10H); ^{13}C NMR: δ 46.9, 77.0, 120.6, 126.1, 127.0, 128.3, 133.6, 146.7; HRMS: calc. for $C_{16}H_{14}$ (M^+-H_2O) 206.1096, found 206.1099.

1-Allyl-cyclohexanol (1m). IR (film): 3385, 3074, 2931, 2855, 1639cm^{-1}; ^{1}H NMR: δ 1.23-1.60 (m, 11H), 2.20 (d, J = 7.2 Hz, 2H), 5.06-5.14 (m, 2H), 5.80-5.94 (m, 1H); ^{13}C NMR: δ 22.3, 25.9, 29.6, 37.5, 71.1, 118.8, 133.9; HRMS: calc. for C_9H_{14} (M^+-H_2O) 122.1096, found 122.1085.

But-3-en-1-ol (1n). IR (film): 3420, 3074, 1639cm^{-1}; ^{1}H NMR: δ 1.12-1.25 (m, 6H), 1.50-1.70 (br, 1H), 1.93-2.05 (br, 1H), 2.10-2.32(m, 2H), 3.62-3.69 (m, 1H), 5.11-5.19 (m, 2H), 5.85-5.94 (m, 1H); ^{13}C NMR: δ 17.2, 17.3, 20.7, 23.5, 40.3, 43.7, 72.5, 73.8, 74.4, 74.7, 118.6, 118.7, 133.6, 133.8; HRMS: calc. for C_7H_{10} (M^+-2H_2O) 94.0783, found 94.0781.

2-Methyl-1-phenyl-but-3-en-1-ol (1o, syn isomer). IR (film): 3417, 3064, 1639cm^{-1}; ^{1}H NMR: δ 0.97 (d, J = 6.8 Hz, 3H), 2.00-2.15 (br, 1H), 2.54-2.58 (m, 1H), 4.54 (d, J = 5.6 Hz, 1H), 4.95-5.00 (m, 2H), 5.65-5.77 (m, 1H), 7.20-7.32 (m, 5H); ^{13}C NMR: δ 16.6, 44.8, 77.4, 115.6, 126.6, 127.4, 128.1, 140.3, 142.4; HRMS: calc. for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1042.

2-Methyl-1-phenyl-but-3-en-1-ol (1o, anti isomer). IR (film): 3417, 3064, 1639cm^{-1}; ^{1}H NMR: δ 0.83 (d, J = 6.8 Hz, 3H), 2.00-2.15 (br, 1H), 2.48-2.52 (m, 1H), 4.31 (d, J = 7.8 Hz, 1H), 5.01-5.12 (m, 2H), 5.65-5.77 (m, 1H), 7.20-7.32 (m, 5H); ^{13}C NMR: δ 14.2, 46.3, 78.0, 116.8, 126.9, 127.7, 128.3, 140.6, 142.6; HRMS: calc. for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1042.

1-(4-Chlorophenyl)-2-methylbut-3-en-1-ol (1p, syn isomer). IR (film): 3406, 2973, 1639cm^{-1}; ^{1}H NMR: δ 0.98 (d, J = 6.8 Hz, 3H), 1.96-2.12 (br, 1H), 2.48-2.57 (m, 1H), 4.58 (d, J = 5.3 Hz, 1H), 5.00-5.08 (m, 2H) , 5.67-5.82 (m, 1H), 7.16-7.31 (m, 4H); ^{13}C NMR: δ 16.5, 44.7, 76.6, 115.9, 127.9, 128.3, 128.5, 133.0, 140.0, 141.2; HRMS: calc. for $C_{11}H_{13}OCl$ (M^+) 196.0655, found 196.0652.

1-(4-Chlorophenyl)-2-methylbut-3-en-1-ol (1p, anti isomer). IR (film): 3406, 2973, 1639cm^{-1}; ^{1}H NMR: δ 0.87 (d, J = 6.7 Hz, 3H), 1.96-2.12 (br, 1H), 2.35-2.46 (m, 1H), 4.33 (d, J = 7.7 Hz, 1H), 5.16-5.21 (m, 2H), 5.67-5.82 (m, 1H), 7.16-7.31 (m, 4H); ^{13}C NMR: δ 14.0, 46.4, 77.2, 117.2, 127.9, 128.3, 128.5, 133.4, 140.3, 141.0; HRMS: calc. for $C_{11}H_{13}OCl$ (M^+) 196.0655, found 196.0652.

2-Methyl-1-(4-methylphenyl)-3-buten-1-ol (1q, syn isomer). IR (film): 3418, 2973, 2871, 1639cm^{-1}; ^{1}H NMR: δ 1.00 (d, J = 6.8 Hz, 3H), 1.98-2.10 (br, 1H), 2.33 (s, 3H), 2.44-2.58 (m, 1H), 4.53 (d, J = 5.6 Hz, 1H), 5.00-5.06 (m, 2H), 5.68-5.86 (m, 1H), 7.14-7.42 (m, 4H); ^{13}C NMR: δ 16.2, 20.8, 44.3, 76.9, 114.9, 126.1, 128.4, 136.6, 139.4, 140.1; HRMS: calc. for $C_{12}H_{16}O$ (M^+)176.1201, found 176.1201.

2-Methyl-1-(4-methylphenyl)-3-buten-1-ol (1q, anti isomer). IR (film): 3418, 2973, 2871, 1639cm^{-1}; ^{1}H NMR: δ 0.85 (d, J = 6.8 Hz, 3H), 1.98-2.10 (br, 1H), 2.33 (s, 3H), 2.44-2.58 (m, 1H), 4.30 (d, J = 7.9 Hz, 1H), 5.14-5.20 (m, 2H), 5.68-5.86 (m, 1H), 7.14-7.42 (m, 4H); ^{13}C NMR: δ 13.9, 20.8, 45.8, 76.3, 116.2, 126.4, 128.5, 136.9, 139.2, 140.5; HRMS: calc. for $C_{12}H_{16}O$ (M^+) 176.1201, found 176.1201.

3-Methyl-2-phenylpent-4-en-2-ol (1r, syn isomer). IR (film): 3477, 2976, 1635cm^{-1}; ^{1}H NMR: δ 0.86 (d, J = 7.0 Hz, 3H), 1.53 (s, 3H), 1.84-2.02 (br, 1H), 2.50-2.62 (m, 1H), 5.08-5.13 (m, 2H), 5.71-5.88 (m, 1H), 7.20-7.44 (m, 5H); ^{13}C NMR: δ 14.9, 28.6, 49.0, 75.9, 116.3, 125.4, 126.6, 128.0, 140.1, 147.2; HRMS: calc. for $C_{12}H_{14}$ (M^+-H_2O) 158.1096, found 158.1098.

3-Methyl-2-phenylpent-4-en-2-ol (1r, anti isomer). IR (film): 3477, 2976, 1635cm^{-1}; ^{1}H NMR: δ 0.96 (d, J = 7.0 Hz, 3H), 1.53 (s, 3H), 1.84-2.02 (br, 1H), 2.50-2.62 (m, 1H), 5.08-5.13 (m, 2H), 5.71-5.88 (m, 1H), 7.20-7.44 (m, 5H); ^{13}C NMR: δ 14.3, 26.1, 49.1, 75.8, 116.6, 125.7, 126.8, 128.0, 140.2, 147.3; HRMS: calc. for $C_{12}H_{14}$ (M^+-H_2O) 158.1096, found 158.1098.

2-(4-Chlorophenyl)-3-methylpent-4-en-2-ol (1s, syn isomer). IR (film): 3454, 1637cm^{-1}; ^{1}H NMR: δ 0.86 (d, J = 6.9 Hz, 3H), 1.52 (s, 3H), 1.76-1.93 (br, 1H), 2.49-2.54 (m, 1H), 5.09-5.16 (m, 2H), 5.75-5.81 (m, 1H), 7.28-7.37 (m, 4H); ^{13}C NMR: δ 14.8, 28.5, 48.9, 75.6, 116.7, 126.9, 128.9, 132.3, 139.6, 145.7; HRMS: calc. for $C_{12}H_{13}Cl$ (M^+-H_2O) 192.0706, found 192.0697.

2-(4-Chlorophenyl)-3-methylpent-4-en-2-ol (1s, anti isomer). IR (film): 3454, 1637cm^{-1}; ^{1}H NMR: δ 0.97 (d, J = 6.9 Hz, 3H), 1.52 (s, 3H), 1.76-1.93 (br, 1H), 2.49-2.54 (m, 1H), 5.09-5.16 (m, 2H), 5.75-5.81 (m, 1H), 7.28-7.37 (m, 4H); ^{13}C NMR: δ 14.2, 26.1, 48.9, 75.6, 116.9, 126.9, 128.9, 132.5, 139.7, 145.7; HRMS: calc. for $C_{12}H_{13}Cl$ (M^+-H_2O) 192.0706, found 192.0697.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (No. 50073021), by the Education Department of Anhui Province (No. 2002kj330zd) and by the Science Foundation of Anhui Province (No. 01046301).

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