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SHORT PAPER

# Gallium-induced Barbier coupling of carbonyl compounds with allyl iodide

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**Gallium metal readily prompted the allylation of aldehydes and ketones with allyl iodide. α,β-Unsaturated carbonyl compounds underwent only 1,2-addition.**

**Keywords: Gallium, allylation, homoallyl alcohol, Barbier reaction, carbonyl compound**

## INTRODUCTION

Recent rapid development in the use of various metallic elements in the field of organic synthetic chemistry has directed attention toward seeking new metals and metal complexes which play unique and important roles in synthetic reactions. In particular, less common metals such as lanthanoids have been attracting increasing interest.[1] Among Group IIIa elements, boron, aluminum and thallium have been well explored and widely used in organic synthesis, whereas gallium and indium have received scant attention.[2] In this paper, we describe how gallium can be used for the Barbier reaction of aldehydes and ketones with allyl iodide (Scheme 1).

## RESULTS AND DISCUSSION

When a mixture of allyl iodide and carbonyl compounds in *N,N*-dimethylformamide (DMF) was ultrasonicated with gallium shavings for 30 min, Barbier coupling occurred smoothly and the corresponding homoallylic alcohols were obtained in good to moderate yields after chromatographic separation. Results are summarized in Table 1.

Aldehydes gave high yields of the coupling products, whereas the reactivity of ketones was somewhat lower. α,β-Unsaturated carbonyl compounds gave only 1,2-addition products. Even salicylaldehyde, which bears a hydroxyl group, gave the coupling product a 91% yield. 4-t-Butylcyclohexanone afforded the corresponding axial alcohol predominantly (axial/equaltorial ratio = 84/16). Allyl bromide is much less reactive than allyl iodide; the reaction with benzaldehyde, for example, gave only 6% of the product. However, in the presence of one equivalent of sodium iodide, the yield increased up to 89%.

The present allylation is highly chemoselective; esters, cyanides, and acyl chlorides could not be allylated under the conditions employed. At present, the nature of the intermediate gallium species of this reaction is not clear; however, organogallium sesquiiodide ($R_3Ga_2I_3$; R=allyl)[3] is the most likely from analogy with the aluminum[4] and indium[5] cases.

Gallium is expensive and Barbier coupling of this type is possible using other metals and metal salt reductants.[6] Nevertheless, the present gallium-mediated allylation is unique because of its generality, high yields, mildness of the reaction conditions, and operational simplicity; it provides a rare example of the use of gallium metal in synthetic chemistry.

## EXPERIMENTAL

Infrared spectra were recorded with a JASCO A-102 spectrometer. $^1$H NMR spectra were measured on a Hitachi R-24A (60 MHz) or a Varian XL-200 (200 MHz) spectrometer using tetramethylsilane as an internal standard. Ultrasonic irradiation was carried out using a Sanyo ultrasonic washer SUW-150 (150 W, 28 kHz).

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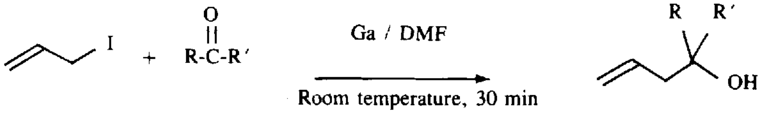
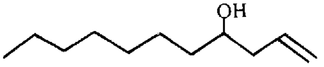
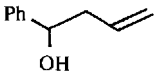
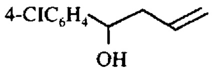
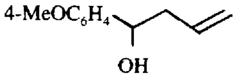
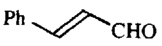
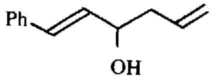
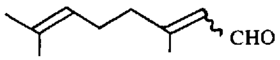
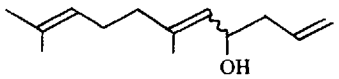
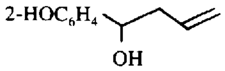
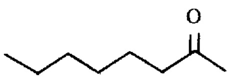
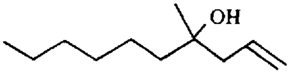
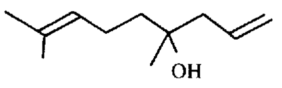
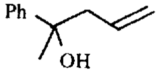
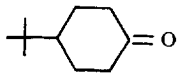
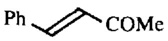
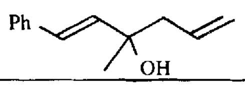


Scheme 1

**Table 1** Gallium-induced allylation of carbonyl compounds[a]

| Carbonyl compound | Product | Yield (%) |
|---|---|---|
|  |  | 88 |
| PhCHO |  | 98 |
| 4-ClC$_6$H$_4$CHO |  | 81 |
| 4-MeOC$_6$H$_4$CHO |  | 83 |
|  |  | 76 |
|  |  | 78 |
| 2-HOC$_6$H$_4$CHO |  | 91 |
|  |  | 75 |
|  |  | 51 |
| PhCOMe |  | 57 |
|  |  | 93[b] |
|  |  | 78 |

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[a] All the reactions were carried out using allyl iodide (2 mmol), carbonyl compound (1 mmol), and gallium (1 mmol) in DMF (1 cm$^3$)

[b] Axial/equatorial alcohol, 84/16.

## Gallium-mediated allylation of carbonyl compounds

Following reaction of benzaldehyde and allyl iodide is representative. Under an argon atmosphere, a mixture of benzaldehyde (106 mg, 1 mmol), allyl iodide (337 mg, 2 mmol), and gallium shavings (70 mg, 1 mmol) in DMF (1 cm$^3$) was ultrasonicated for 30 min. During this period, the gallium shavings were consumed and a clear mixture was obtained. The reaction was quenched by the addition of dilute (1 mol dm$^{-3}$) hydrochloric acid and the product was extracted with ether. The extracts were washed successively with saturated aqueous sodium hydrogencarbonate ($NaHCO_3$), water, and brine, and then dried over anhydrous sodium sulfate. The ether solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluant: dichloromethane) to furnish 1-phenyl-3-buten-1-ol (145 mg, 98% yield). Other reactions were similarly carried out and the structures of the products were deduced by their spectral data. All the products are known compounds,[6] so only their IR and $^1$H NMR data are given below.

### 1-Undecen-4-ol

IR (neat): 3370, 3080, 2935, 2875, 1644, 1466, 1456, 994, 912 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 0.88 (t, *J* = 7 Hz, 3H, Me), 1.23–1.56 (m, 12H, $CH_2$), 2.08 (bs, 1H, OH), 2.13–2.38 (m, 2H, $CH_2$), 3.58–3.73 (m, 1H, CH), 5.13 (dd, *J* = 10, 1 Hz, 1H, olefin H), 5.14 (dd, *J* = 16, 1 Hz, 1H, olefin H), 5.75–5.96 (m, 1H, olefin H).

### 1-Phenyl-3-buten-1-ol

IR (neat): 3400, 3100, 3050, 2950, 2925, 1644, 1496, 1454, 1050, 1002, 918, 760, 702 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 2.44 (t, *J* = 6 Hz, 2H, $CH_2$), 2.65 (bs, 1H, OH), 4.64 (t, *J* = 6 Hz, 1H, CH), 5.10 (d, *J* = 11 Hz, olefin H), 5.11 (d, *J* = 16 Hz, 1H, olefin H), 5.66–5.86 (m, 1H, olefin H), 7.24–7.38 (m, 5H, Ph).

### 1-(4-Chlorophenyl)-3-buten-1-ol

IR (neat): 3380, 3090, 2950, 2920, 1642, 1494, 1092, 1050, 1016, 920, 832 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 2.25 (t, *J* = 7 Hz, 2H, $CH_2$), 3.35 (bs, 1H, OH), 4.43 (t, *J* = 7 Hz, 1H, CH), 4.87–5.04 (m, 2H, olefin H), 5.47–5.67 (m, 1H, olefin H), 6.98–7.23 (m, 4H, Ar).

### 1-(4-Methoxyphenyl)-3-buten-1-ol

IR (neat): 3420, 3080, 3020, 2940, 2845, 1614, 1516, 1248, 1176, 1036, 918, 832 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 2.45 (t, *J* = 6 Hz, 2H, $CH_2$), 2.57–2.77 (m, 1H, OH), 3.75 (s, 3H, OMe), 4.61 (t, *J* = 6 Hz, 1H, CH), 5.08 (d, *J* = 17 Hz, 1H, olefin H), 5.66–5.88 (m, 1H, olefin H), 6.87 (d, *J* = 9 Hz, 2H, Ar), 7.25 (d, *J* = 9 Hz, 2H, Ar).

### (E)-1-Phenyl-1,5-hexadien-3-ol

IR (neat): 3370, 3080, 3030, 2930, 2920, 1642, 1496, 1448, 1028, 968, 916, 746, 692 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 2.37 (t, *J* = 6 Hz, 2H, $CH_2$), 3.00 (bs, 1H, OH), 4.30 (bq, *J* = 6 Hz, 1H, CH), 5.11 (d, *J* = 10 Hz, 1H, olefin H), 5.13 (d, *J* = 16 Hz, 1H, olefin H), 5.72–5.96 (m, 1H, olefin H), 6.21 (dd, *J* = 16, 6 Hz, 1H, olefin H), 6.56 (d, *J* = 16 Hz, 1H, olefin H), 7.15–7.42 (m, 5H, Ph).

### 6,10-Dimethyl-1,5,9-undecatrien-4-ol

IR (neat): 3370, 3110, 3000, 2950, 1646, 1444, 1380, 1028, 1004, 916 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 1.61 (s, 3H, Me), 1.68 (bs, 6H, Me), 1.96–2.38 (m, 7H, $CH_2$ and OH), 4.43 (bq, *J* = 7 Hz, 1H, CH), 5.06–5.32 (m, 4H, olefin H), 5.70–5.95 (m, 1H, olefin H).

### 1-(2-Hydroxyphenyl)-3-buten-1-ol

IR (neat): 3360, 3100, 3060, 3000, 2980, 2965, 1644, 1590, 1494, 1458, 1244, 1036, 990, 922, 756 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 2.52 (bt, *J* = 7 Hz, 2H, $CH_2$), 4.04 (bs, 1H, OH), 4.80 (t, *J* = 7 Hz, 1H, CH), 5.08 (d, *J* = 11 Hz, 1H, olefin H), 5.09 (d, *J* = 16 Hz, 1H, olefin H), 5.64–5.85 (m, 1H, olefin H), 6.74–7.18 (m, 4H, Ar), 8.36 (bs, 1H, OH).

### 4-Methyl-1-decen-4-ol

IR (neat): 3420, 3110, 2970, 2880, 1644, 1470, 1460, 1380, 1158, 1144, 1002, 918 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 0.89 (t, *J* = 6 Hz, 3H, Me), 1.16 (s, 3H, Me), 1.23–1.60 (m, 11H, $CH_2$ and OH), 2.23 (d, *J* = 7 Hz, 2H, $CH_2$), 5.06–5.23 (m, 2H, olefin H), 5.78–5.99 (m, 1H, olefin H).

### 4,8-Dimethyl-1,7-nonadien-4-ol

IR (neat): 3410, 3080, 2980, 2935, 1642, 1452, 1448, 1376, 1116, 998, 914 cm$^{-1}$; $^1$H NMR ($CDCl_3$): 1.18 (s, 3H, Me), 1.43–1.54 (m, 2H, $CH_2$), 1.62 (s, 3H, Me), 1.69 (s, 3H, Me), 1.79 (bs, 1H, OH), 1.99–2.14 (m, 2H, $CH_2$), 2.24 (d, $J = 7$ Hz, 2H, $CH_2$), 5.05–5.22 (m, 3H, olefin H), 5.77–5.98 (m, 1H, olefin H).

### 2-Phenyl-4-penten-2-ol

IR (neat): 3435, 3085, 3070, 3035, 2985, 2935, 1640, 1494, 1444, 1374, 1068, 1028, 998, 012, 764, 698 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): 1.48 (s, 3H, Me), 2.39–2.69 (m, 3H, $CH_2$ and OH), 5.00–5.14 (m, 2H, olefin H), 5.51–5.74 (m, 1H, olefin H), 7.14–7.47 (m, 5H Ph).

### 1-Allyl-4-t-butylcyclohexanol (axial alcohol)

IR (neat): 3400, 3080, 2975, 2950, 2875, 2850, 1638, 1476, 1440, 1390, 1364, 1234, 1188, 1140, 992, 952, 912 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): 0.86 (s, 9H, Me), 1.24–1.79 (m, 10H, $CH_2$, CH, and OH), 2.18 (d, $J = 7$ Hz, 2H, $CH_2$), 5.03–5.19 (m, 2H, olefin H), 5.79–6.00 (m, 1H, olefin H).

### 1-Allyl-4-t-butylcyclohexanol (equatorial alcohol)

IR (neat): 3400, 3080, 2975, 2950, 2875, 1638, 1476, 1466, 1450, 1392, 1364, 1228, 1144, 1036, 990, 910 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): 0.86 (s, 9H, Me), 1.08–1.86 (m, 10H, $CH_2$, CH, and OH), 2.31 (d, $J = 7$ Hz, 2H, $CH_2$), 5.09–5.28 (m, 2H, olefin H), 5.80–6.02 (m, 1H, olefin H).

### (E)-3-Methyl-1-phenyl-1,5-hexadien-3-ol

IR (neat): 3420, 3085, 3075, 3035, 2980, 2935, 2820, 1640, 1598, 1494, 1446, 1434, 1370, 1272, 1102, 970, 916, 748, 694 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): 1.33 (s, 3H, Me), 2.25–2.45 (m, 2H, $CH_2$), 2.62 (bs, 1H, OH), 5.04–5.17 (m, 2H, olefin H), 5.72–5.94, (m, 1H, olefin H), 6.25 (d, $J = 16$ Hz, 1H, olefin H), 6.58 (d, $J = 16$ Hz, 1H, olefin H), 7.12–7.38 (m, 5H, Ph).

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