**SHORT PAPER**

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# Highly regioselective nucleophilic addition of the allylsamarium bromide to α, β-unsaturated alkynones[†]

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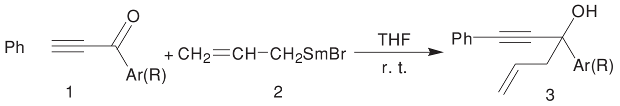
Allylsamarium bromide reacts with α, β-unsaturated alkynones to afford reginospecific nucleophilic addition products in good yields under mild conditions.

**Keywords:** allylsamarium bromide α, β-unsaturated alkynones

The addition of allylic organometallics to carbonyl compounds is an important synthetic method for the construction of carbon–carbon bonds.[1] Usually, homoallylic alcohols were obtained utilising these methods, and little attention has been paid to the geminal diallylation of carbonyl compounds.[2] Since Curran reported the samarium Grignard reaction,[3] our group has developed progressively allylsamarium bromide and explored its Grignard-type reactions. For example, allylselenides, allylsulfides, homoallylamines, butenamides, thiobutenamides, tertiary amides, homoallyl alcohols were synthesised by reaction of diselenides, disulfides, nitriles, isothiocyanide, isocyanates, adducts of Schiff bases and acyl chlorides, aldehydes, ketones, esters, α, β-unsaturated aldehydes and ketones with allylsamarium bromide.[4, 5–7]



**Scheme 1**

Herein we wish to report that the allylsamarium bromide reacts with α, β-unsaturated alkynones to afford reginospecific nucleophilic addition products in good yields (Scheme 1).

According to previous reports, in the case of Grignard reagents, both 1,2- and 1,4-additions were possible,[8,9] the orientation depended on some effects such as the bulk of the substrates and reagents. Although many researches have been carried out on the subject by different authors no absolute conclusion can be reached.[9] Furthermore, the preparation of allylmagnesium bromide is not effective because of coupling reactions. When allylmagnesium bromide reacts with α, β-unsaturated alkynketones, we found that the results were unsatisfactory. The 1,2-and 1,4-addition products were obtained together and the yields were low. It is interesting that allylsamarium bromide reacts with α, β-unsaturated alkynketones to afford reginospecific nucleophilic 1, 2-addition products in good yields under mild condition. The results are shown on Table 1.

In conclusion, the nucleophilic addition of allylsamarium bromide to an alkynone is regiospecific, speedy and gives high yields at room temperature. The products are of multi-functional groups of widely synthetic application. The mild reaction conditions, readily available starting materials, simple operations and high yields make this method potentially valuable.

**Table 1** The results of the reaction of allylsamarium bromide and α, β-unsaturated alkynone

| Entry | Ar(R) | t/h(min) [a] | T/°C[b] | Products | Yields/%[c] |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | 10 | r. t. | **3a** | 96 |
| 2 | $p$-$CH_3C_6H_4$ | 10 | r. t. | **3b** | 94 |
| 3 | $p$-$CH_3OC_6H_4$ | 10 | r. t. | **3c** | 88 |
| 4 | $p$-$ClC_6H_4$ | 10 | r. t. | **3d** | 95 |
| 5 | 2-$ClC_6H_4$ | 10 | r. t. | **3e** | 86 |
| 6 | 2, 6-$Cl_2C_6H_3$ | 10 | r. t. | **3f** | 82 |
| 7 | Furanyl | 10 | r. t. | **3g** | 88 |
| 8 | $CH_3CH_2CH_2$ | 10 | r. t. | **3h** | 83 |

[a]reaction time, [b]reaction temperature, [c]isolated yields.

## Experimental

Melting points were uncorrected. IR spectra were recorded on a Bruker Vector-22 infrared spectrometer. $^1H$ NMR spectra were obtained with a Bruker AC-400 MHz spectrometer in $CDCl_3$ or DMSO-$d_6$ solution using TMS as the internal standard. Mass spectra were recorded on an HP 5989B MS spectrometer. Elemental analyses were performed on a Carlo Erba 1106 instrument. The reactions were performed in a Schlenk-type glass apparatus under a nitrogen atmosphere. The starting unsaturated alkynones was prepared from the oxidation of aryl prop-2-yn-1-ol with activated manganese dioxide according to ref.10.

*General procedure for the nucleophilic addition reaction of allylsamarium bromide to α, β-unsaturated alkynones*: Under a nitrogen atmosphere, samarium (0.165g, 1.1mmol) and allyl bromide (0.15g, 1.2mmol) in THF (15ml) were added to a three-necked flask with stirring at room temperature under dinitrogen. When the colour of the mixture turned to purple, stirring was continued for one hour until the samarium powder disappeared, then the α, β-unsaturated alkynone (1mmol) was added to the solution, and the mixture was stirred at room temperature for ten minutes. 2ml 0.1N HCl and 5ml water were added. The reaction mixture was extracted with diethyl ether (3×10ml), the diethyl ether solution was washed with saturated $Na_2S_2O_3$ (10ml), then washed with water (10ml) and dried over anhydrous $Na_2SO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane-ethyl acetate (8:1) as eluent).

*Compound* **3a**: oil. $\delta_H$ (ppm) 7.72–7.70 (d, 2H, $J$=8Hz), 7.50–7.47 (m, 2H), 7.41–7.36 (m, 2H), 7.33–7.30 (m, 4H), 6.04–5.94 (m, 1H), 5.23–5.18 (t, 2H), 2.82–2.71 (m, 2H), 2.67 (s, 1H). $\nu_{max}$ (KBr)/cm$^{-1}$: 3422, 3061, 3031, 2979, 2912, 1640, 1598, 1490, 1447, 1029, 918, 757, 691. MS: $m/z$, 247 (M-1, 0.16), 231 (2.53), 207 (100), 189 (1.88), 129 (75.67), 105 (31.94), 77 (37.17), 41 (16.27). Anal. calcd. for $C_{18}H_{16}O$: C 87.06, H 6.49%, Found: C 87.10, H 6.47%

*Compound* **3b**: oil. $\delta_H$ (ppm) 7.56–7.58 (d, 2H, $J$=8Hz), 7.46–7.48 (d, 2H, $J$=8Hz), 7.24–7.32 (m, 3H), 5.95–5.97 (m, 1H), 5.16–5.21 (t, 2H), 2.72–2.76 (m, 2H), 2.60 (s, 1H), 2.35 (s, 3H). $\nu_{max}$ (KBr)/cm$^{-1}$: 3424, 3077, 3024, 2979, 2920, 1640, 1598, 1573, 1510, 1442, 1179, 1022, 917, 819, 756, 691. MS: $m/z$, 262 (M$^+$, 0.22), 261 (M-1, 0.45), 247 (2.4), 246 (21.20), 245 (100), 221 (73.71), 222 (13.74), 129 (95.59), 119 (27.58), 91 (31), 41 (39.44). Anal. calcd. for $C_{19}H_{18}O$: C 86.98, H 6.92%, Found: C 86.97, H 6.90%.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

*Compound* **3c**: oil. $\delta_H$ (ppm) 7.62–7.66 (d, 2H, *J*=8Hz), 7.49–7.51 (d, 2H, *J*=8), 7.36–7.33 (m, 3H), 6.91–6.95 (d, 2H, *J*=16Hz), 5.95–6.02 (m, 1H), 5.18–5.24 (t, 2H), 3.84 (s, 3H), 2.76–2.79 (m, 2H), 2.72 (s, 1H). $\nu_{max}$ (KBr)/$cm^{-1}$: 3444, 3076, 2935, 2836, 1640, 1609, 1510, 1249, 1174, 1035, 832, 757, 691. MS: *m*/*z*, 261 (M-17, 100), 262 (21.90), 237 (98.64), 208 (1.90), 176 (2.66), 165 (14.53), 135 (49.44), 129 (97.49), 115 (6.09), 101 (7.80), 77 (20.74), 41 (50.16). Anal. calcd. for $C_{19}H_{18}O_2$: C 81.98, H 6.52%, Found: C 81.95, H 6.55%.

*Compound* **3d**: oil. $\delta_H$ (ppm) 7.63–7.65 (d, 2H, *J*=8Hz), 7.48–7.50 (d, 2H, *J*=8Hz), 7.35–7.38 (m, 5H), 5.96–5.98 (m, 1H), 5.18–5.26 (t, 2H), 2.72–2.77 (m, 2H), 2.68 (s, 1H). $\nu_{max}$ (KBr)/$cm^{-1}$: 3416, 3079, 2980, 2914, 1641, 1597, 1575, 1488, 1401, 1092, 1014, 918, 830, 756, 690. MS: *m*/*z*, 279 (4.14), 278 (5.25), 277 (24.60), 276 (13.61), 275 (37.14), 274 (11.80), 248 (27.42), 246 (44.23), 176 (25.30), 177 (8.10), 175 (31.25), 174 (8.23), 173 (40.14), 129 (100), 109 (12.14), 101 (17.56), 77 911.42), 51 (25.30), 41 (22.53). Anal. calcd. for $C_{18}H_{15}ClO$: C 76.45, H 5.34, Cl 12.54%, Found: C 76.49, H 5.33, Cl 12.52%.

*Compound* **3e**: oil. $\delta_H$ (ppm) 7.62–7.64 (d, 2H, *J*=8Hz), 7.61–7.28 (m, 6H), 7.12–7.16 (m, 1H), 5.98–6.05 (m, 1H), 5.25–5.29 (t, 2H), 3.33 (s, 1H), 3.19–3.12 (m, 2H). $\nu_{max}$ (KBr)/$cm^{-1}$: 3543, 3078, 2980, 2923, 1658, 1576, 1560, 1430, 1286, 1204, 1108, 1026, 1011, 920, 778, 796, 689. MS: *m*/*z*, 268 (3.22), 267 (16.7), 266 (10.73), 265 (47.37), 243 (30.06), 241 (87.46), 244 (4.68), 242 (16.57), 189 (2.45), 187 (2.02), 178 (3.69), 177 (3.17), 176 (6.99), 175 (1.38), 141 (16.30), 139 (49.52), 129 (100), 111 (25.27), 75 (29.57), 41 (47.37). Anal. calcd. for $C_{18}H_{15}ClO$: C 76.45, H 5.34, Cl 12.54%, Found: C 76.47, H 5.38, Cl 12.55%.

*Compound* **3f**: oil. $\delta_H$ (ppm) 7.61–7.63 (d, 2H, *J*=8Hz), 7.61–7.64 (m, 3H), 7.33–7.15 (m, 3H), 6.21–6.18 (m, 1H), 5.23–5.26 (t, 2H), 3.20–3.18 (m, 2H) 3.43 (s, 1H). $\nu_{max}$ (KBr)/$cm^{-1}$: 3466, 3072, 2987, 2889, 1647, 1576, 1542, 1437, 1254, 1108, 1075, 932, 766, 676. MS: *m*/*z*, 318 (0.12), 316 (0.61), 302 (2.48), 301 (2.55), 300 (4.02), 299 (100), 275 (77.45), 274 (22.56), 273 (33.20), 272 (16.88), 263 (66.51), 262 (25.60), 173 (47.55), 175 (62.86), 145 (24.88), 147 (16.10), 109 (14.77), 77 (31.64), 51 (19.11), 50 (10.94). Anal. calcd. for $C_{18}H_{14}Cl_2O$: C 68.15, H 4.45, Cl 22.35%, Found: C 68.11, H 4.49, Cl 22.36%

*Compound* **3g**: oil. $\delta_H$ (ppm) 7.49–7.51 (d, 2H, *J*=8Hz), 78.44–7.48(d, 1H, *J*=16Hz), 7.33–7.36 (m, 3H), 6.52–6.53 (t, 1H), 6.37–6.38 (d, 1H, *J*=4Hz), 5.94–6.01 (m, 1H), 5.22–5.26 (t, 2H), 2.94–2.96 (d, 2H, *J*=16Hz), 2.74 (s, 1H). $\nu_{max}$ (KBr)/$cm^{-1}$: 3422, 3079, 2980, 2918, 1639, 1597, 1566, 1489, 1443, 1224, 1154, 1010, 918, 756, 691. MS: *m*/*z*, 237 (M-1), 198 (14.87), 197 (100), 139 (10.97), 129 (43.46), 115 (13.36), 95 (91.80), 75 (12.44), 77 (9.78), 41 (25.31). Anal. calcd. for $C_{16}H_{14}O_2$: C 80.64, H 5.92%, Found: C 80.65, H 5.95%

*Compound* **3h**: oil. $\delta_H$ (ppm) 7.26–7.28 (d, 2H, *J*=8Hz), 7.13–7.16(m, 3H), 5.87–5.94 (m, 1H), 5.05–5.10 (t, 2H), 2.42–2.47 (m, 1H), 2.32–2.27 (m, 1H), 2.17 (s, 1H), 1.56–1.61 (t, 2H), 1.49–1.53 (m, 2H), 0.83–0.87 (t, 3H). $\nu_{max}$ (KBr)/$cm^{-1}$: 3424, 3078, 2959, 2873, 1640, 1598, 1489, 1442, 1124, 1022, 991, 916, 756, 690. MS: *m*/*z*, 214 ($M^+$, 0.63), 213 (0.60), 197 (100), 173 (13.28), 155 (21.57), 141 (6.47), 129 (12.49), 115 (6.23), 105 (2.74), 77 (2.85), 41 (28.27). Anal. calcd. for $C_{15}H_{18}O$: C 84.06, H 8.46%, Found: C 84.10, H 8.42%.

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