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Three-component coupling of acetylenic sulfones, Grignard reagents and α, β-unsaturated carbonyls: A convenient synthesis of diallylic alcohols

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ABSTRACT

A convenient synthesis of diversely substituted diallylic alcohols is developed *via* Cu-mediated three-component coupling reaction of acetylenic sulfones, Grignard reagents and α, β-unsaturated carbonyls. Polysubstituted diallylic alcohols containing a sulfonyl group could be obtained in up to 85% yield.

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1. Introduction

Allylic alcohols are common structural motifs in natural occurring and biologically active compounds [1]. Allylic alcohols are also important synthetic intermediates in organic chemistry due to the versatile reactivity of carbon-carbon double bond and hydroxyl group. For example, allylic alcohols are applied in many organic syntheses such as transition-metal catalyzed allylation reactions [2], Claisen rearrangements and related sigmatropic processes [3], redox reactions [4], and other transformations [5]. Therefore, development of new methods to synthesis allylic alcohols is in high demand [6]. The coupling reactions between alkynes and carbonyl compounds provide a direct access to allylic alcohols and aldehydes are the mostly used coupling partners [7]. However, synthesis of tertiary allylic alcohols by using ketones as the coupling partners remains relatively unexplored [1a,8].

Diallylic alcohols, members of allylic alcohols, are also potential intermediates in organic synthesis. Recently, the Nazarov cyclization of diallylic alcohols attracted great interest of chemists [9]. Although the synthesis of allylic alcohols has been extensively studied, there are only sporadic reports of the synthesis of diallylic alcohols [9b-9d]. As part of our research interest in the stereoselective synthesis of functionalized polysubstituted alkenes from alkynes [10], we wish to report herein the three-component coupling reaction of acetylenic sulfones, Grignard reagents and α, β-unsaturated carbonyls, which provides a simple and convenient synthesis of diallylic alcohols.

2. Results and discussion

Previously, we have reported the stereoselective synthesis of tetrasubstituted vinyl sulfones by Cu(I)-promoted carbomagnesiation of acetylenic sulfones and its further reaction with electrophiles [11]. According to the reported procedure, the three-component reaction of acetylenic sulfones, Grignard reagents and α, β-unsaturated carbonyls was investigated under the similar reaction conditions. At 0 °C, acetylenic sulfone (**1**) was added to the solution of 1.2 equiv of Grignard reagent (**2**) in Et_2O/CH_2Cl_2 in the presence of 10 mol% of CuCN. After the consumption of acetylenic sulfone, 1.2 equiv of α, β-unsaturated carbonyl (**3**) was added. Diallylic alcohols **4** were obtained after purification, which were formed by tandem carbomagnesiation-aldol reaction of acetylenic

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sulfones, Grignard reagents and α, β-unsaturated carbonyls. The results are summarized in Table 1.

From Table 1 we can see that the reaction is quite general and differently substituted diallylic alcohols **4** could be synthesized by this method. The R^1 in acetylenic sulfones **1** can be phenyl or *n*-butyl. The R^2 in Grignard reagents **2** can be ethyl (Table 1, entries 1–8), benzyl (Table 1, entries 9–15), *n*-butyl (Table 1, entries 16–21) allyl (Table 1, entries 22–26) or phenyl (Table 1, entry 27). α, β-Unsaturated ketones were well tolerated in the reaction and the R^3 can be a phenyl, *p*-chlorophenyl, *p*-methoxyphenyl or *p*-nitrophenyl, and the R^4 can be a phenyl or methyl. The similar reaction of cinnamaldehyde (**3g**) was also investigated and the corresponding products (**4g**, **4o,** and **4z'**) were obtained (Table 1, entries 7, 15 and 27). As revealed in Table 1, in the case of R^4 being phenyl, the yield of **4** is lower than that of R^4 being methyl, which may be due to the steric effect of phenyl. When R^3 is *p*-chlorophenyl, products **4** were obtained in 55–82% yields. However, a relatively lower yields (lower than 50%) of **4** were obtained in the case of R^3 being *p*-methoxyphenyl, which may owned to the electronic effect of methoxyl and chloro.

The three-component reaction proceeded in high regio- and stereoselectivity. The molecular structures of compounds **4e** and **4l** were confirmed by the X-ray diffraction analysis (Fig. 1) [12]. From Fig. 1 we can see the addition of Grignard reagents **2** to acetylenic sulfones **1** proceeded in the *syn*-fashion to form α-sulfonyl vinylmagnesium bromide intermediates **I**, which react with α, β-unsaturated carbonyls to give 1,2-adducts **4**.

3. Conclusion

In summary, we have developed a convenient three-component tandem reaction for the construction of diallylic alcohols from acetylenic sulfones, Grignard reagents and α, β-unsaturated carbonyls. The resulting diallylic alcohols would be highly useful intermediates for organic synthesis because of the versatile carbon-carbon double bond, sulfonyl and hydroxyl groups.

4. Experimental

4.1. General experimental procedure for the synthesis of diallylic alcohols *4*

A Schlenk flask was charged with 0.5 mmol (128 mg) of 1-phenyl-2-(*p*-tosyl)ethyne (**1a**), 0.6 mmol of ethylmagnesium bromide (**2a**), 0.05 mmol (4.5 mg) of CuCN and 5 mL of Et_2O/CH_2Cl_2 (v/v 2/3) under argon atmosphere. The reaction mixture was stirred at 0 °C. After the full consumption of **1a** (monitored by TLC), 0.6 mmol (146 mg) of (*E*)-3-(*p*-chlorophenyl)-1-phenylpropenone (**3a**) was added and the reaction mixture was stirred for 4 h at 0 °C. The reaction was then quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent *in vacuo*, the crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/15) to give the product **4a**.

4.2. (1E,4Z)-1-(4-chlorophenyl)-3,5-diphenyl-4-tosylhepta-1,4-dien-3-ol (*4a*)

White solid. m.p. 176–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.46–7.33 (m, 7H), 7.26–7.09 (m, 5H), 7.02–6.92 (m, 3H), 6.85–6.80 (m, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 5.65 (s, 1H), 2.45–2.35 (m, 5H), 0.27 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7, 145.3, 144.4, 142.8, 139.8, 138.8, 134.9, 133.6, 129.1, 129.0, 128.8, 128.7, 128.5, 128.3, 127.9, 127.7, 127.6, 127.4, 127.2, 126.5, 80.7, 33.0, 21.4, 10.6. IR (KBr): *v* (cm^{-1}) 3439, 3061, 2924, 1582, 1489, 1377, 1279, 1136, 927. HRMS (ESI) $[M+Na]^+$: *m/z* calcd for $C_{32}H_{29}ClNaO_3S$: 551.1424, found: 551.1391.

4.3. (1E,4Z)-1,3,5-triphenyl-4-tosylhepta-1,4-dien-3-ol (*4b*)

White solid. m.p. 74–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.45–7.31 (m, 7H), 7.23–7.10 (m, 4H), 7.08–6.96 (m, 4H), 6.87–6.77 (m, 3H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.64 (s, 1H), 2.47–2.27 (m, 5H), 0.25 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7, 145.7, 144.5, 142.9, 140.1, 139.0, 136.5, 132.8, 130.4, 128.9, 128.7, 128.6, 128.3, 128.0, 127.9, 127.7, 127.4, 127.3, 126.9, 126.7, 80.7, 33.2, 21.5, 10.6. IR (KBr): *v* (cm^{-1}) 3453, 3059, 2967, 1597, 1449, 1375, 1279, 1138, 974. HRMS (APCI) $[M+H]^+$: *m/z* calcd for $C_{32}H_{31}O_3S$: 495.1994, found: 495.1987.

4.4. (1E,4Z)-1-(4-methoxyphenyl)-3,5-diphenyl-4-tosylhepta-1,4-dien-3-ol (*4c*)

White solid, m.p. 86–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 6.9 Hz, 2H), 7.48–7.32 (m, 5H), 7.25–7.08 (m, 5H), 7.02–6.88 (m, 5H), 6.80–6.69 (m, 2H). 6.65 (d, *J* = 15.8 Hz, 1H), 5.62 (s, 1H), 3.83 (s, 3H), 2.35 (m, 5H), 0.23 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 157.6, 145.8, 144.7, 142.9, 140.1, 139.0, 130.7, 130.0, 129.2, 129.1, 128.9, 128.5, 128.4, 128.1, 127.8, 127.6, 127.4, 126.7, 114.1, 80.8, 55.3, 33.2, 21.5, 10.6. IR (KBr): *v* (cm^{-1}) 3472, 3030, 2974, 1607, 1512, 1443, 1252, 1136, 976. HRMS (APCI) $[M+H]^+$: *m/z* calcd for $C_{33}H_{33}O_4S$: 525.2100, found: 525.2091.

4.5. (1E,4Z)-3-methyl-1,5-diphenyl-4-tosylhepta-1,4-dien-3-ol (*4d*)

White solid. m.p. 125–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.35–7.26 (m, 5H), 7.19–7.04 (m, 5H), 6.91–6.76 (m, 3H), 6.65 (d, *J* = 16.2 Hz, 1H), 4.95 (s, 1H), 2.64–2.55 (m, 1H), 2.47–2.36 (m, 4H), 1.99 (s, 3H), 0.67 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 145.0, 142.8, 140.6, 139.3, 136.5, 135.0, 129.4, 129.0, 128.7, 128.1, 127.9, 127.6, 127.5, 127.0, 126.7, 75.7, 32.7, 29.3, 21.5, 11.8. IR (KBr): *v* (cm^{-1}) 3516, 3024, 2932, 1585, 1442, 1359, 1279, 1136, 905. HRMS (APCI) $[M+H]^+$: *m/z* calcd for $C_{27}H_{29}O_3S$: 433.1837, found: 433.1830.

4.6. (1E,4Z)-1-(4-chlorophenyl)-3-methyl-5-phenyl-4-tosylhepta-1,4-dien-3-ol (*4e*)

White solid. m.p. 117–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.27 (m, 6H), 7.16–7.04 (m, 5H), 6.95–6.85 (m, 1H), 6.79–6.60 (m, 3H), 4.97 (s, 1H), 2.61–2.55 (m, 1H), 2.45–2.36 (m, 4H), 1.99 (s, 3H), 0.65 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 145.0, 142.9, 140.4, 139.2, 135.7, 135.0, 133.5, 129.3, 129.2, 129.0, 128.1, 127.9, 127.7, 127.5, 127.0, 75.7, 32.6, 29.2, 21.5, 11.8. IR (KBr): *v* (cm^{-1}) 3528, 3067, 2972, 1709, 1580, 1493, 1375, 1283, 1142, 970. HRMS (ESI) $[M+Na]^+$: *m/z* calcd for $C_{27}H_{27}ClNaO_3S$: 489.1267, found: 489.1233.

4.7. (1E,4Z)-1-(4-methoxyphenyl)-3-methyl-5-phenyl-4-tosylhepta-1,4-dien-3-ol (*4f*)

White solid. m.p. 120–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.33 (m, 4H), 7.19–7.04 (m, 5H), 6.91–6.86 (m, 3H), 6.77–6.72 (m, 2H), 6.50 (d, *J* = 16.2 Hz, 1H), 4.89 (s, 1H), 3.82 (s, 3H), 2.64–2.57 (m, 1H), 2.47–2.40 (m, 1H), 2.36 (s, 3H), 1.96 (s, 3H), 0.66 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 156.3, 145.1, 142.7, 140.6, 139.3, 132.9, 129.0, 128.9, 128.8, 128.0, 127.8, 127.4, 127.3, 126.9, 114.0, 75.6, 55.2, 32.6, 29.2, 21.4, 11.7. IR (KBr): *v* (cm^{-1}) 3509, 2974, 1607, 1512, 1360, 1279, 1136, 966. HRMS (APCI) $[M+H]^+$:

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