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An Efficient Double 1,2-Addition Reaction of 2,3-Allenoates with Allyl Magnesium Chloride

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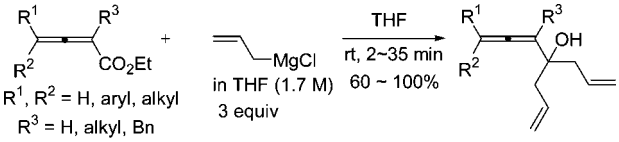
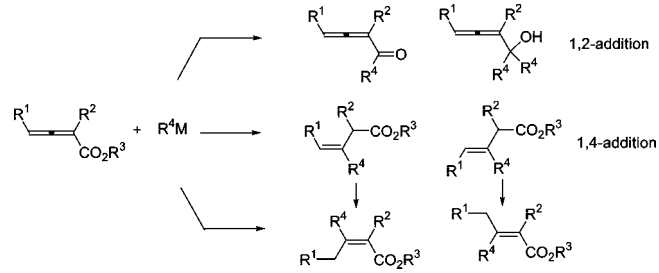


In this paper, it was reported that double 1,2-addition reaction of 2,3-allenoates with allyl magnesium chloride at room temperature in the absence of any transition metal catalyst provides an efficient method for the synthesis of tertiary α-allenols. The optically active allenol could be prepared from the reaction of the optically active 2,3-allenoate without obvious racemization of the axial chirality. Under different reaction conditions, cyclization reactions of α-allenol **2i** prepared have been studied for the synthesis of different 2,5-dihydrofuran derivatives.

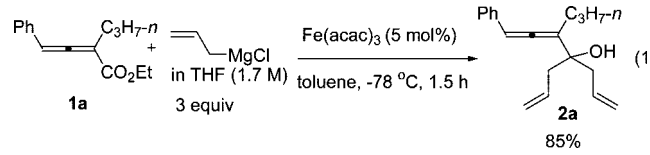
During the last 20 years, due to the high reactivity, substituent-loading capability and the stereochemistry involved in the chemistry of allenes, many chemists focus their attention on the development of new reactions of functionalized allenes.[1] On the basis of these developments, allenes have become powerful starting materials in organic chemistry. Thus, new methods for efficient synthesis of allenes are of current interest.

Due to the possible 1,2-addition, 1,4-addition, and migration of the carbon−carbon double bond, the reaction of 2,3-allenoates with main group organometallic reagents may provide different products (Scheme 1). Herein, we wish to report our recent observation that the reaction of 2,3-allenoates with allyl magnesium chloride affords the double allylation products, that is, synthetically useful 2,3-allenols.[2]

SCHEME 1



Recently, we have realized an iron-catalyzed highly regio- and stereoselective conjugate addition reaction of 2,3-allenoates with alkyl, aryl or alkenyl Grignard reagents providing an efficient route to β,γ-unsaturated alkenoates with excellent stereoselectivity.[3] However, when we tested the similar iron-catalyzed reaction of ethyl 4-phenyl-2-(*n*-propyl)- 2,3-butadienoate **1a** with allyl magnesium chloride in a solution of toluene at −78 °C, the double 1,2-addition product, i.e., tertiary 2,3-allenol **2a**, was formed in 85% isolated yield (eq 1). The formation of the 1,4-addition product was not observed.



Subsequently, the 1,2-addition reaction of ethyl 4-(*p*-bromophenyl)-2-propyl-2,3-butadienoate **1b** with allyl magnesium chloride was conducted at −78 °C in the absence of the iron catalyst to afford the similar alcohol product **2b** (entry 1, Table 1). The reaction could also take place in toluene, THF, or Et_2O to afford **2b** in very similar yields. Considering the operational simplicity, safety, and the yield for the formation of **2b** (entries 2−4, Table 1), we defined the reaction of 0.4 mmol of 2,3-allenoates with 3 equiv of allyl magnesium chloride in a solution of THF (5 mL) at room temperature as the standard (entry 3, Table 1).

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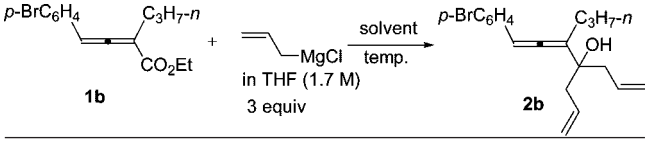
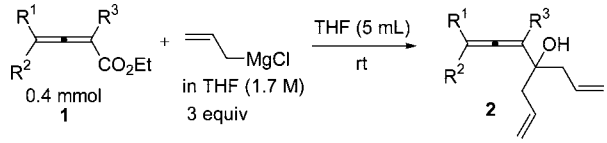
TABLE 1. Effect of Temperature and Solvents on the Reaction of 2,3-Allenoate 1b with Allyl Magnesium Chloride



entry	solvent	*T* (°C)	time (min)	NMR yield of **2b** (%)
1	toluene	−78	51	86
2	toluene	rt	52	90
3	THF	rt	33	91
4	Et_2O	rt	26	89

TABLE 2. Reaction of 2,3-Allenoates with Allyl Magnesium Chloride

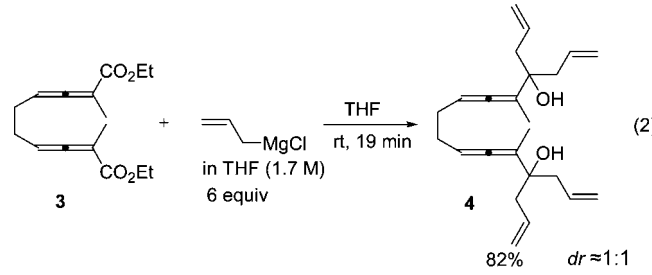


	1				
entry	R^1	R^2	R^3	time(min)	isolated yield of **2** (%)
1	Ph	H	*n*-Pr (**1a**)	3	94 (**2a**)
2	*p*-BrC_6H_4	H	*n*-Pr (**1b**)	33	95 (**2b**)
3	Ph	H	Me (**1c**)	20	85 (**2c**)
4	*p*-ClC_6H_4	H	Me (**1d**)	4	90 (**2d**)
5	*p*-FC_6H_4	H	Me (**1e**)	19	88 (**2e**)
6	*p*-$MeOC_6H_4$	H	Me (**1f**)	3	79 (**2f**)
7	Ph	H	Et (**1g**)	4	94 (**2g**)
8	*n*-C_4H_9	H	Me (**1h**)	4	86 (**2h**)
9	*n*-C_4H_9	H	Bn (**1i**)	8	100 (**2i**)
10[a]	*n*-C_4H_9	H	Bn (**1i**)	4	97 (**2i**)
11	Ph	Ph	H (**1j**)	3	83 (**2j**)
12	*n*-C_7H_{15}	H	H (**1k**)	6	97 (**2k**)
13	Ph	Me	Me (**1l**)	33	97 (**2l**)
14	Ph	Et	Me (**1m**)	3	91 (**2m**)
15	Ph	Ph	Me (**1n**)	2	90 (**2n**)
16	Et	Et	Me (**1o**)	35	60 (**2o**)
17	$(CH_2)_5$		Me (**1p**)	3	94 (**2p**)
18[a]	H	H	Me (**1q**)	2	63 (**2q**)
19[b]	H	H	H (**1r**)	20	64 (**2r**)

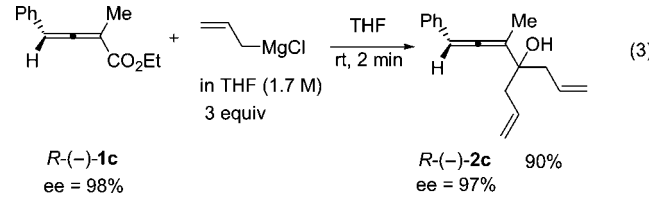
[a] The reaction was run with 2 mmol of 2,3-allenoate. [b] The allenoate **1r** was methyl 2,3-butadienoate.

Under the optimized reaction conditions, a wide range of the substrates were tested and the results are summarized in Table 2. The data shown in Table 2 indicated that the reactions are fast, efficient, and general (Table 2) at room temperature in the absence of any transition metal catalyst: R^1 and R^2 can be aryl, alkyl, and Bn in 2,4-disubstituted 2,3-allenoates (entries 1−10, Table 2); 4,4-Diphenylbutadienoate **1j** and undeca-2,3-dienoate **1k** may also react smoothly to afford the corresponding alcohols **2j** and **2k** in 83% and 97% yields, respectively (entries 11 and 12, Table 2). The fully substituted 2,3-allenoates **1l**−**1q** all reacted with allyl magnesium chloride smoothly (entries 13−17, Table 2). However, the reaction of 4-unsubstituted ethyl 2-methyl-2,3-butadienoate **1q** and methyl 2,3-butadienoate **1r** with allyl magnesium chloride afforded the 1,2,6-heptatrien-4-ols **2q** and **2r** in much lower yields (63% and 64%, respectively) (entries 18 and 19, Table 2).

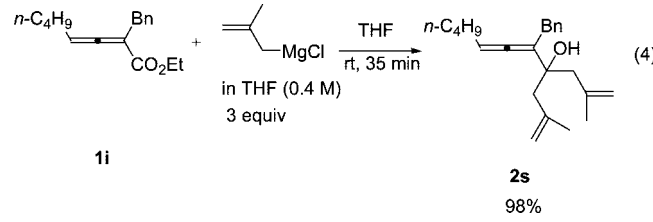
The reaction of diethyl 2,9-dimethyl-2,3,7,8-decatetraenedioate **3** with 6 equiv of allyl magnesium chloride afforded the tetraallyl-substituted bis-allenol **4** in 82% yield (eq 2).



In addition, optically active allenol (*R*)-**2c** can be prepared in 90% isolated yield from optically active (*R*)-**1c**[4] without obvious racemization of the axial chirality (eq 3).



The reaction may also proceed with 2-methylallyl magnesium chloride[5a] (eq 4).



However, the reaction of **1i** with 1-buten-3-yl, 2-butenyl, 3-phenyl-2-propenyl[5b] magnesium chlorides all afforded complicated mixtures probably due to the issue of regioselectivity.

Finally, it should be noted that under the standard reaction conditions, the reaction of 2-benzylocta-2,3-dienoate **1i** with vinyl magnesium chloride in THF is complicated; the corresponding reaction with methyl or phenyl magnesium chloride in THF at room temperature yielded the related conjugated addition products.[3]

Under different cyclization conditions,[6] the prepared 4-allyl-5-benzyl-1,5,6-undecatrien-4-ol **2i** can easily be converted to different 2,5-dihydrofuran derivatives in 76∼99% yields (Scheme 2). Due to the presence of two allyl groups, 2,5-dihydrofuran **7** may undergo a RCM reaction[7] to form an extra five-membered ring to afford bicyclic compound **8** in 86% yield (Scheme 2).

In conclusion, we have established a protocol for the efficient and general preparation of tertiary 1,1-diallyl substituted-2,3-allenols in high yields via the reaction of 2,3-allenoates with allyl magnesium chlorides at room tempreture. The optically active allenol may be prepared from the reaction of the optically active 2,3-allenoate with allyl magnesium chloride without obvious racemization of the axial chirality. The products have been applied to the synthesis of 2,5-dihydrofuran derivatives.

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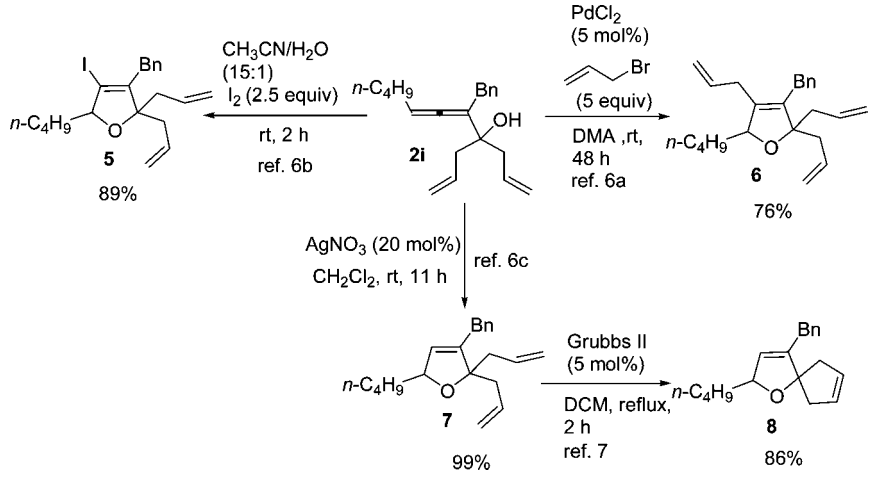
SCHEME 2



Due to the synthetic potential of the 2,3-allenols, this reaction may be useful in organic synthesis. Further studies in this area are being conducted in our laboratory.

Experimental Section

Materials. Toluene, Et_2O, and THF were distilled from Na/benzophenone. 2,3-Allenoates were prepared according to the known procedure.[8] Allyl magnesium chloride (1.7 M solution in THF) used in this study was purchased from Acros Organics. 1-Buten-3-yl magnesium chloride and 2-butenyl magnesium chloride (0.5 M solution in THF) used in this study were purchased from Aldrich Organics. 2-Methylallyl magnesium chloride (0.4 M solution in THF) and 3-phenyl-2-propenyl magnesium chloride (0.4 M solution in Et_2O) used in this study were prepared according to the known procedures.[5] Other commercially available chemicals were purchased and used without additional purification unless noted otherwise.

Synthesis of 2,3-Allenols via the Reaction of 2,3-Allenoates in THF with Allyl Magnesium Chloride in THF. Synthesis of 4-Allyl-1-phenyl-3-(*n*-propyl)-1,2,6-heptatrien-4-ol (2a). To a solution of **1a** (92.5 mg, 0.4 mmol) in THF (5 mL) in a dry Schlenk tube under a nitrogen atmosphere at room temperature was added a solution of allyl magnesium chloride in THF (0.7 mL, 1.7 M, 1.2 mmol, 3 equiv) by a syringe at rt. The reaction was monitored by TLC. After 3 min, the reaction mixture was quenched slowly with saturated NH_4Cl (1 mL) at rt and extracted with ether (60 mL). The organic layer was washed subsequently with diluted HCl (1%, aq.), $NaHCO_3$ (sat. aq.), brine, and dried over anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded **2a** (101.8 mg, 94%): oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.33−7.26 (m, 4 H), 7.28−7.20 (m, 1 H), 6.28 (t, J = 3.3 Hz, 1 H), 5.92−5.70 (m, 2 H), 5.15−5.00 (m, 4 H), 2.45−2.25 (m, 4 H), 2.10−1.90 (m, 3 H), 1.50−1.33 (m, 2 H), 0.86 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 200.7, 134.9, 133.8, 133.5, 128.6, 126.9, 126.6, 118.60, 118.58, 114.6, 99.4, 74.7, 44.1, 43.8, 29.9, 21.1, 14.2; MS (*m*/*z*) 268 (M^+, 2.17), 250 ($(M-H_2O)^+$, 6.24), 227 ($(M-C_3H_5)^+$, 41.00), 41 ($C_3H_5^+$, 100); IR (neat) 3560, 3475, 3076, 3030, 2958, 2931, 2872, 1943, 1639, 1598, 1496, 1459, 1436, 1340, 1028 cm^{-1}; HRMS calcd for $C_{19}H_{24}O$ (M^+) 268.1827, found 268.1830.

Synthesis of 2,5-Dihydrofuran Derivatives via Cyclization Reactions of α-Allenol 2i. (1) Synthesis of 2,2-Diallyl-3-benzyl-5-butyl-4-iodo-2,5-dihydrofuran (5). A solution of **2i** (58.9 mg, 0.2 mmol) and I_2 (131.0 mg, 0.5 mmol, 2.5 equiv) in CH_3CN (2 mL) and H_2O (0.13 mL) was stirred at rt. When the reaction was complete as monitored by TLC, the mixture was then quenched with a saturated aqueous solution of $Na_2S_2O_3$ to remove the excess I_2. This mixture was extracted with ether (3 × 25 mL), washed with an aqueous solution of NaCl, and dried over Na_2SO_4. Concentration and column chromatography on silica gel (First: petroleum ether, then: petroleum ether/ethyl acetate = 40:1) afforded **5** (74.4 mg, 89%): oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.40−7.18 (m, 5 H), 5.72−5.54 (m, 2 H), 5.02−4.84 (m, 4 H), 4.65−4.59 (m, 1 H), 3.55 (d, J = 15.0 Hz, 1 H), 3.46 (dd, J_1 = 15.0 Hz, J_2 = 1.4 Hz, 1 H), 2.26 (ddt, J_1 = 14.4 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1 H), 2.18−2.07 (m, 3 H), 1.94−1.82 (m, 1 H), 1.56−1.28 (m, 5 H), 0.92 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 145.9, 137.4, 133.5, 133.2, 128.9, 128.4, 126.7, 117.8, 96.5, 93.0, 87.8, 43.9, 43.1, 35.5, 34.9, 27.0, 22.7, 14.1; MS (*m*/*z*) 381 ($(M - C_3H_5)^+$, 56.03), 254 ($(M - C_3H_5-I)^+$, 100); IR (neat) 3075, 3027, 2956, 2930, 2858, 1640, 1601, 1494, 1454, 1432, 1331, 1100 cm^{-1}; Elemental analysis: Calcd for $C_{21}H_{27}IO$: C, 59.72; H, 6.44; Found: C, 59.85; H, 6.40.

(2) Synthesis of 2,2,4-Triallyl-3-benzyl-5-butyl-2,5-dihydrofuran (6). A solution of **2i** (89.0 mg, 0.3 mmol), allyl bromide (188.0 mg, 1.5 mmol, 5 equiv), and $PdCl_2$ (3.0 mg, 0.015 mmol) in DMA (1 mL) was stirred at rt. When the reaction was complete as monitored by TLC, this mixture was added with ether (60 mL). The organic layer was washed subsequently with diluted HCl (1%, aq.), $NaHCO_3$ (sat. aq.), brine, and dried over anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel (First: petroleum ether, then: petroleum ether/ethyl acetate = 100/1) afforded the desired product **6** (76.8 mg, 76%): liquid. ^{1}H NMR (300 MHz, $CDCl_3$) 7.32−7.13 (m, 5 H), 5.82−5.60 (m, 3 H), 5.13−4.85 (m, 6 H), 4.72−4.60 (m, 1 H), 3.43 (d, J = 15.9 Hz, 1 H), 3.30 (d, J = 15.9 Hz, 1 H), 3.02−2.90 (m, 1 H), 2.67 (dd, J = 15.6 Hz, J = 7.2 Hz, 1 H), 2.40−2.28 (m, 1 H), 2.22−2.08 (m, 3 H), 1.74−1.56 (m, 1 H), 1.50−1.23 (m, 5 H), 0.91 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 138.9, 136.1, 134.7, 134.6, 134.4, 134.3, 128.8, 128.3, 126.2, 117.2, 117.0, 116.2, 92.3, 85.4, 44.2, 43.1, 34.5, 31.3, 30.1, 27.7, 22.9, 14.1; MS (*m*/*z*) 295 ($(M - C_3H_5)^+$, 100); IR (neat) 3075, 3027, 3007, 2957, 2929, 2858, 1830, 1639, 1603, 1495, 1454, 1432, 1377, 1335, 1259, 1076, 1016 cm^{-1}; Elemental analysis: Calcd for $C_{24}H_{32}O$: C, 85.66; H, 9.58; Found: C, 85.63; H, 9.57.

(3) Synthesis of 2,2-Diallyl-3-benzyl-5-butyl-2,5-dihydrofuran (7). A solution of **2i** (58.9 mg, 0.2 mmol) and $AgNO_3$ (6.9 mg, 0.04 mmol, 20 mol%) in CH_2Cl_2 (2 mL) was stirred at rt. When the reaction was complete as monitored by TLC, ether (10 mL) was added to quench the reaction. Concentration and column chromatography on silica gel (First: petroleum ether, then: petroleum ether/ethyl acetate = 100:1) afforded **7** (58.5 mg, 99%): liquid. ^{1}H NMR (300 MHz, $CDCl_3$) 7.40−7.14 (m, 5 H), 5.94−5.75 (m, 2 H), 5.15−4.98 (m, 5 H), 4.62−4.54 (m, 1 H), 3.23−3.10 (m, 2

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H), 2.52−2.27 (m, 4 H), 1.55−1.45 (m, 1 H), 1.40−1.20 (m, 5 H), 0.86 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 143.7, 138.7, 134.4, 134.1, 129.4, 128.3, 126.4, 126.2, 117.1, 91.7, 84.8, 43.4, 43.2, 36.6, 33.4, 27.9, 22.8, 14.0; MS (*m*/*z*) 255 ($(M - C_3H_5)^+$, 100); IR (neat) 3073, 3028, 2956, 2928, 2858, 1640, 1605, 1496, 1454, 1432, 1118, 1029 cm^{-1}; Elemental analysis: Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52; Found: C, 85.11; H, 9.54.

(4) Synthesis of 4-Benyl-2-(*n*-butyl)-1-oxaspiro[4.4]nona-3,7-diene (8). The Grubbs II catalyst (9.2 mg, 0.01mmol) was added to a solution of **7** (41.8 mg, 0.2 mmol, 5 mol%) in CH_2Cl_2 (4 mL) under a N_2 atmosphere. After being stirred under reflux conditions for 2 h as monitored by TLC, the resulting solution was concentrated and purified by flash column chromatography on silica gel (petroleum ether/Et_2O = 100:1) to give **8** (32.5 mg, 86%): liquid. ^{1}H NMR (300 MHz, $CDCl_3$) 7.35−7.28 (m, 2 H), 7.27−7.18 (m, 3 H), 5.75−5.68 (m, 2 H), 5.15−5.10 (m, 1 H), 4.75−4.65 (m, 1 H), 3.28−3.23 (m, 2 H), 2.67−2.44 (m, 4 H), 1.54−1.40 (m, 2 H), 1.38−1.20 (m, 4 H), 0.87 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 144.5, 139.0, 129.1, 128.7, 128.5, 128.3, 126.2, 125.1, 96.5, 83.5, 45.3, 43.9, 36.4, 33.2, 27.3, 22.8, 14.0; MS (*m*/*z*) 268 (M^+, 34.32), 211 ($(M - C_4H_9)^+$, 100); IR (neat) 3060, 3028, 2956, 2928, 2857, 1659, 1614, 1603, 1496, 1454, 1466, 1431, 1378, 1331, 1300, 1260, 1211, 1113, 1085, 1030 cm^{-1}; Elemental analysis: Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01; Found: C, 85.06; H, 9.04.

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Supporting Information Available: Experimental details and ^{1}H/^{13}C NMR spectra of all the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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