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Journal of Organometallic Chemistry 692 (2007) 505–513
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Gallium-mediated allyl transfer from bulky homoallyl alcohol to aldehydes or alkynes: Control of dynamic σ-allylgalliums based on retro-allylation reaction

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Received 6 February 2006; received in revised form 15 March 2006; accepted 20 March 2006
Available online 30 August 2006

Abstract

A new method for the preparation and control of dynamic σ-allylgalliums is disclosed. Upon treatment with a Grignard reagent and gallium trichloride, bulky homoallyl alcohols undergo gallium-mediated retro-allylation reaction to provide σ-allylgallium reagents. The σ-allylgallium reagents generated were applied to carbonyl allylation. The retro-allylation reaction generates (*Z*)- and (*E*)-σ-crotylgalliums stereospecifically, starting from *erythro*- and *threo*-homoallyl alcohols, respectively. The stereochemically defined crotylgallium reagents effected stereoselective allylation of aldehydes. Allylgallation reaction of alkynes with the allylgallium reagents prepared by retro-allylation is also described.

Keywords: Gallium; Retro-allylation; σ-Allylgallium; Allylation; Carbon–carbon bond cleavage

1. Introduction [1]

Preparations of allylmetals have been well investigated because of their importance in organic synthesis [2]. In addition to conventional preparations such as Barbier–Grignard-type reductive metalation and transmetalation of a highly reactive allyl metal to other metals, retro-allylation of metal homoallyloxide also generates allylmetals [3]. However, its application to organic synthesis is rare [4]. Here we report a method for the generation of allylgallium reagents by gallium-mediated retro-allylation reaction of bulky homoallyl alcohols and its application [5,6].

2. Results and discussion

2.1. Gallium-mediated allyl transfer from bulky homoallyl alcohol to aldehydes via retro-allylation: Stereoselective synthesis of both erythro- and threo-homoallyl alcohols

Treatment of homoallyl alcohol **1a** (1.2 mmol) with methylmagnesium iodide (1.2 mmol) in dioxane yielded the magnesium alkoxide of **1a** (Scheme 1). Gallium trichloride (1.2 mmol) and benzaldehyde (1.0 mmol) were added to the suspension at 25 °C. Stirring the resulting suspension for 0.5 h provided homoallyl alcohol **2a** in 94% yield. The reaction showed no *erythro*/*threo* selectivity. A substoichiometric amount (40 mol%) of gallium trichloride also effected the crotylation reaction [7], affording **2a** in 79% yield. The use of 20 mol% of gallium trichloride led to a low yield of **2a** and formation of benzyl alcohol as a byproduct through a Meerwein–Ponndrof–Verley reduction. A significant drop of the yield was observed when

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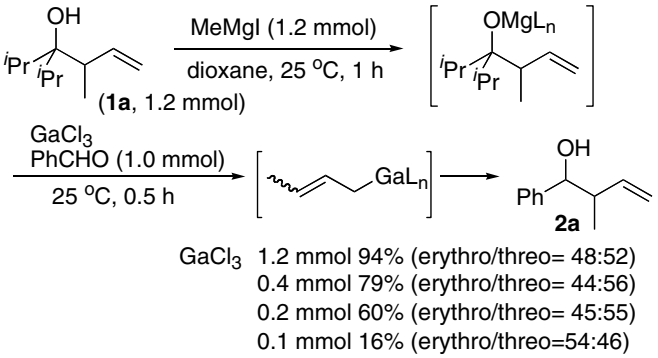
doi:10.1016/j.jorganchem.2006.08.047



Scheme 1.

10 mol% of gallium trichloride was employed. Methylmagnesium iodide is suitable as a base. Butyllithium instead of methylmagnesium iodide did not promote the reaction, and the starting materials were completely recovered. Methylmagnesium bromide served as efficiently as methylmagnesium iodide (93% yield, *erythro*/*threo* = 48:52). Cesium carbonate in place of methylmagnesium iodide did not function as a base. Gallium trichloride was much more effective than indium trichloride. A similar reaction with indium trichloride provided a 71% yield of **2a** (*erythro*/*threo* = 44:56).

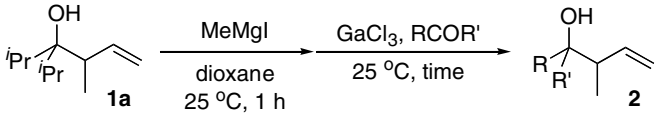
The regioselectivity of the reaction suggests that the allyl transfer reaction proceeds via a mechanism completely different from the Lewis acid-mediated allyl transfer reactions reported by Nokami and others [8]. Formation of σ-crotylgallium species by retro-crotylation is most probable. Stereoselective allyl transfer reaction as well as allylgallation of alkyne also justifies the retro-allylation mechanism (*vide infra*).

A variety of aldehydes were subjected to the crotylation reaction (Table 1). Aliphatic aldehydes as well as aromatic ones underwent the crotylation reaction. Crotylation of cyclohexanecarbaldehyde exhibited with high *threo* selectivity (entry 3). The reaction of pivalaldehyde yielded a mixture of the desired product and linear homoallyl alcohol, 2,2-dimethyl-5-hepten-3-ol, probably due to the steric hindrance of the *t*-butyl group (entry 4). Selective 1,2-addition was observed in the reaction of α,β-unsaturated aldehydes (entries 5 and 6). The crotylation of an aldehyde moiety predominated over that of ester (entry 7). The reactions with ketones furnished the corresponding tertiary alcohols in good yield (entries 8 and 9).

The retro-allylation reaction could generate other allylgallium reagents (Table 2). Unsubstituted allyl transfer furnished the desired product **2k** in good yield albeit a longer reaction time was necessary for completion (entry 1). Methallylation proceeded as smoothly as the crotylation to provide **2l** in excellent yield (entry 2). However, prenylation was not efficient starting from diisopropyl-substituted **1d** (entry 3). Instead, dimethyl substitution at the oxygenated carbon strongly enhanced the prenylation (entry 4). Delicate steric factors around the hydroxy groups play a crucial role in these allyl transfer reactions.

Paying attention to the delicate steric effect, we further investigated the crotylation reaction by using other crotyl sources. We found that homoallyl alcohol **1f**, which has mesityl and methyl groups at its hydroxylated carbon, participated in the crotyl transfer reaction in ether even at −20 °C. To our delight, the reaction showed stereospecificity when diastereomerically pure **1f** was used. Namely, the reactions of *erythro*-**1f** and *threo*-**1f** with benzaldehyde provided *erythro*- and *threo*-**2a**, respectively (Scheme 2). Other aromatic aldehydes underwent the stereospecific crotylation reaction (Table 3, entries 1–6). The reactions with dihydrocinnamaldehyde and cinnamaldehyde resulted in lower stereoselectivity (entries 7–10).

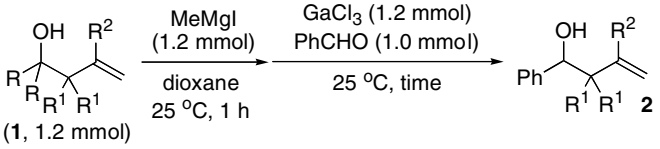
Table 1
Crotylation of various carbonyl compounds via retro-crotylation[a]



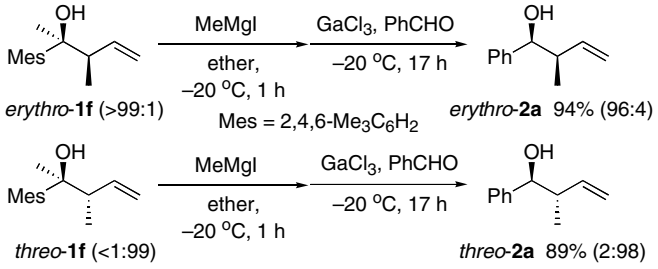
Entry	RCOR′	Time (h)	**2**	Yield (%)	*erythro*/*threo*
1	*p*-$CH_3C_6H_4CHO$	1.5	**2b**	88	48:52
2	$PhCH_2CH_2CHO$	1	**2c**	72	55:45
3	$^cC_6H_{11}CHO$	0.5	**2d**	99	12:88
4	$^tC_4H_9CHO$	3	**2e**	45[b]	48:52
5	(*E*)-PhCH=CHCHO	3	**2f**	70[c]	54:46
6	(*E*)-$^nC_8H_{17}CH$=CHCHO	3	**2g**	71[c]	52:48
7	*p*-MeOC(=O)C_6H_4CHO	2.5	**2h**	85	42:58
8	Cyclohexanone	0.5	**2i**	59	–
9	Acetophenone	1	**2j**	57[d]	53:47

[a] Performed as described in Scheme 1 by using 1.2 equiv. of $GaCl_3$.
[b] Linear homoallyl alcohol, 2,2-dimethyl-5-hepten-3-ol, was obtained in 13% yield.
[c] Performed in ether at 0 °C. Conversion of α,β-unsaturated aldehyde under the standard conditions resulted in a lower yield because of the concomitant formation of the corresponding triene that followed the crotylation.
[d] Linear homoallyl alcohol, 2-phenyl-4-hexen-2-ol, was obtained in 8% yield.

Table 2
Allylation, methallylation, and prenylation of benzaldehyde



Entry	1	R	R^1	R^2	Time (h)	2	Yield (%)
1	**1b**	^{i}Pr	H	H	13	**2k**	68
2	**1c**	^{i}Pr	H	Me	0.5	**2l**	94
3	**1d**	^{i}Pr	Me	H	11	**2m**	32
4	**1e**	Me	Me	H	1	**2m**	78



Scheme 2.

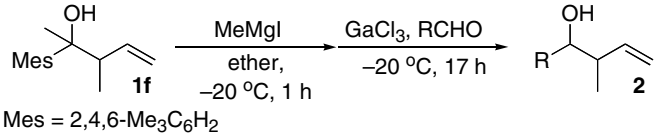
We rationalize the stereospecific allyl transfer as outlined in Scheme 3. Upon the retro-crotylation reaction of *erythro*-**1f**, a chair transition state **3a** would be most stable, because of the least steric demand, in comparison to other possible transition states such as another chair transition state **3b**. Formation of the (*Z*)-σ-crotylgallium reagent is thus favored. The (*Z*)-σ-crotylgallium reagent probably reacts so rapidly with benzaldehyde in the same pot that its isomerization into the (*E*)-form is limited. Aliphatic aldehyde **2c** and α,β-unsaturated aldehyde **2f** are less reactive. The lower reactivity allowed the (*Z*)-σ-crotylgallium reagent to isomerize into the (*E*)-σ-crotylgallium (Table 3, entries 7–10). The crotylation of benzaldehyde would proceed via a cyclic transition state, which selectively provides *erythro*-**2a**. Starting from *threo*-**1f**, an (*E*)-σ-crotylgallium reagent would be predominantly generated via **4a** and led to *threo*-**2a**.

Attempted NMR analysis of the retro-allylation process failed. For instance, ^{1}H and ^{13}C NMR analysis of a mixture of methylmagnesium iodide, **1a**, and gallium trichloride showed no detectable crotylgallium reagents. The overall allyl transfer process is likely to be in equilibrium. Once the crotylgallium is formed, it would immediately react with carbonyl compounds of less steric hindrance.

Homopropargyl alcohol **1g** transferred the propargyl moiety to aldehydes (Scheme 4). In contrast, allenylation of benzaldehyde with **1h** resulted in the formation of a complex mixture including **2r** and **2p**. Transfer from homoallyl alcohol **1i** to benzaldehyde suffered from very low conversion, albeit the regioselectivity was good.

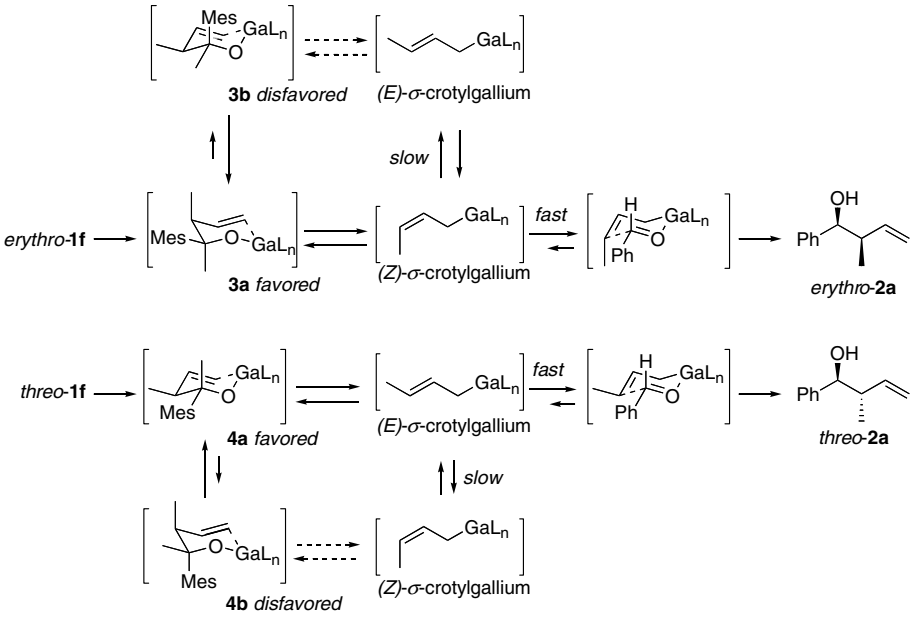
Stereoselective preparations of σ-crotylmetals represent an important challenge. Stereochemically defined σ-crotylmetals should always be prepared in advance of the crotylation reaction. Our new method utilizes stable and easy-to-handle homoallyl alcohols as the precursors of a σ-crotylmetal. The first selective generations of (*E*)- and

Table 3
Selective synthesis of *erythro*- and *threo*-homoallyl alcohols



Entry	1f	R	2	Yield (%)	*erythro*/*threo* of 2
1	*erythro*	*p*-$CF_3C_6H_4$	**2n**	84	96:4
2	*threo*	*p*-$CF_3C_6H_4$	**2n**	92	2:98
3	*erythro*	*o*-ClC_6H_4	**2o**	87	99:1
4	*threo*	*o*-ClC_6H_4	**2o**	83	3:97
5	*erythro*	*p*-$CH_3C_6H_4$	**2b**	95[a]	98:2
6	*threo*	*p*-$CH_3C_6H_4$	**2b**	64[a]	2:98
7	*erythro*	$PhCH_2CH_2$	**2c**	87	69:31
8	*threo*	$PhCH_2CH_2$	**2c**	62	42:58
9	*erythro*	PhCH=CH	**2f**	86	91:9
10	*threo*	PhCH=CH	**2f**	66	21:79

[a] Reaction time was 30 h.



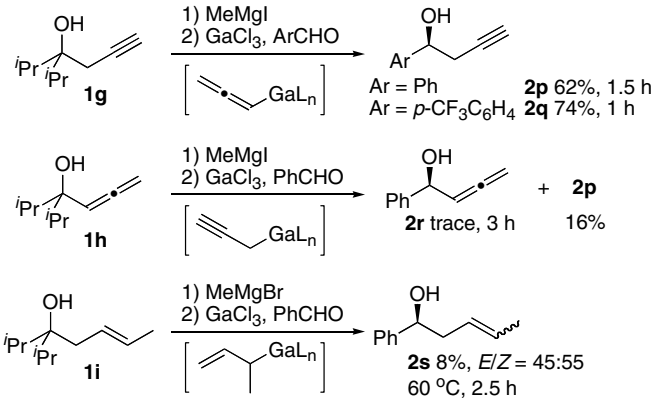
Scheme 3.

(*Z*)-σ-crotylgallium were established *in situ* via the gallium-mediated retro-allylation.

2.2. Allylgallation of alkynes with allylgallium reagents generated by retro-allylation

Allylgallation of alkynes is among the most interesting reactions in organogallium chemistry [9]. As described above, we proposed the generation of crotylgallium reagents by retro-allylation. To confirm the generation of the crotylgallium reagents, allylgallation reaction of alkynes with homoallyl alcohol via retro-allylation was examined.

As anticipated, the allylgallation with homoallyl alcohol proceeded smoothly (Table 4). Homoallyl alcohol **1a** was treated with methylmagnesium iodide and gallium trichloride in dioxane. Alkyne **5a** was added to the suspension, and the whole mixture was heated at reflux for 2 h. The reaction was terminated with aqueous hydrochloric acid to give **6a** in excellent yield (entry 1). The regioselectivity



Scheme 4. The conditions were the same as those in Table 1.

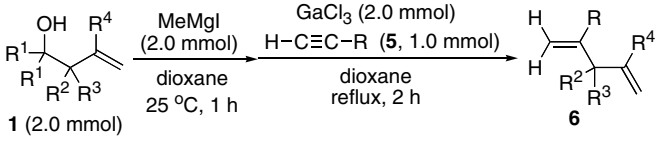
of the reaction is the same as previously reported [9]. It is worth noting that the highly coordinating amino moiety of **5d** did not retard the allylgallation. Not only crotylation but also allylation (entries 6 and 7) and methallylation (entries 8–12) were successful. Methallylation of alkynes generally led to high yields. Unfortunately, attempted prenylation encountered very low conversion (entries 13 and 14). Aliphatic acetylene **5e** as well as arylacetylenes undergo the allylation reaction (entries 5 and 12). The reactions of **5a** with **1a** in the presence of 40 mol% and 20 mol% of gallium trichloride provided **6a** in 23% and 7% yields, respectively.

When the reaction was quenched with DCl, a mixture of **6g**, monodeuterated (***E***)-**6g-d_1**, and dideuterated **6g-d_2** was obtained (Scheme 5). Furthermore, allylgallation of 1-phenyl-2-deuterioacetylene followed by quench with HCl afforded **6g** and (***Z***)-**6g-d_1**. The results of these two experiments can be explained by the reaction mechanism as depicted in Scheme 6. Allylgallation of phenylacetylene proceeds via a six-membered transition state **7a** to produce vinylgallium **8a**. The vinylgallium **8a** is partially quenched with alkyne in situ to afford **6g** with no deuterium incorporation. The remaining **8a** reacted with DCl upon workup to give (***E***)-**6g-d_1**. Meanwhile, deprotonation of the acetylenic proton of phenylacetylene takes place by the action of basic gallium species. The gallium acetylide **5b-Ga** undergoes allylgallation to provide 1,1-dimetalated alkene **8b**. Deuteriolysis of **8b** provided **6g-d_2**.

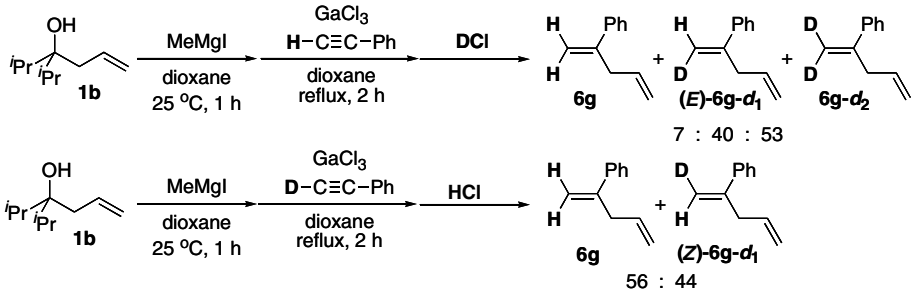
3. Summary

Stereoselective preparations and uses of σ-allylmetals represent an interesting challenge since σ-allylmetals are generally dynamic complexes that are difficult to control, except for allylmetals of group 14 and allylboranes. As

Table 4
Allylgallation of terminal alkynes with homoallyl alcohol via retro-allylation



Entry	1	R^1	R^2	R^3	R^4	5	R	6	Yield (%)
1	**1a**	^{i}Pr	Me	H	H	**5a**	*p*-$MeOC_6H_4$	**6a**	96
2	**1a**	^{i}Pr	Me	H	H	**5b**	C_6H_5	**6b**	43[a]
3	**1a**	^{i}Pr	Me	H	H	**5c**	*p*-FC_6H_4	**6c**	35[a]
4	**1a**	^{i}Pr	Me	H	H	**5d**	*p*-$Me_2NC_6H_4$	**6d**	57
5	**1a**	^{i}Pr	Me	H	H	**5e**	$^n C_{10}H_{21}$	**6e**	49[a]
6	**1b**	^{i}Pr	H	H	H	**5a**	*p*-$MeOC_6H_4$	**6f**	52
7	**1b**	^{i}Pr	H	H	H	**5b**	C_6H_5	**6g**	81
8	**1c**	^{i}Pr	H	H	Me	**5a**	*p*-$MeOC_6H_4$	**6h**	99
9	**1c**	^{i}Pr	H	H	Me	**5b**	C_6H_5	**6i**	94
10	**1c**	^{i}Pr	H	H	Me	**5c**	*p*-FC_6H_4	**6j**	71
11	**1c**	^{i}Pr	H	H	Me	**5d**	*p*-$Me_2NC_6H_4$	**6k**	66
12	**1c**	^{i}Pr	H	H	Me	**5e**	$^n C_{10}H_{21}$	**6l**	85
13	**1e**	Me	Me	Me	H	**5a**	*p*-$MeOC_6H_4$	**6m**	41
14	**1e**	Me	Me	Me	H	**5b**	C_6H_5	**6n**	13[a]



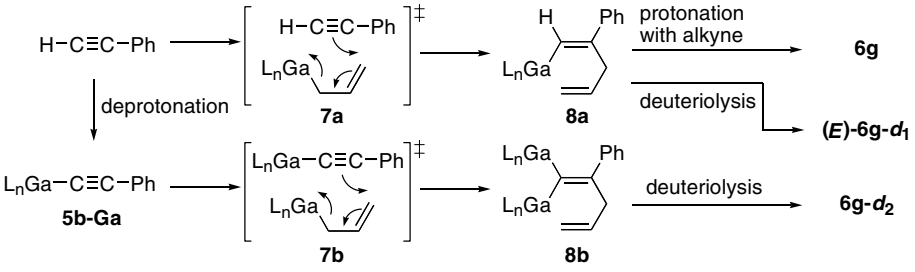
Scheme 5.

illustrated in the Section 2.1, our retro-allylation strategy offers control of σ-allylmetals and will be applicable to synthesis of other σ-allylmetals [10].

4. Experimental

4.1. Instrumentation and chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.23 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.



Scheme 6.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aldehydes were purified by distillation prior to use. Methylmagnesium iodide was prepared from magnesium metal and iodomethane in ether. Dioxane was purchased from Wako Pure Chemical Co. and stored over slices of sodium. Gallium trichloride was purchased from Aldrich and was diluted in a grove box under argon to prepare 1.0 M hexane solution. All reactions were carried out under argon atmosphere.

4.2. Typical procedure for allyl transfer reaction via allylgallium reagent (Scheme 1)

A solution of **1a** (0.204 g, 1.20 mmol) in 1,4-dioxane (10 mL) was placed in a 30-mL reaction flask. Methylmagnesium iodide (1.0 M ether solution, 1.20 mL, 1.2 mmol) was added dropwise to the solution at ambient temperature. After the mixture was stirred for 1 h, gallium trichloride (1.0 M hexane solution, 1.20 mL, 1.2 mmol) and benzaldehyde (0.106 g, 1.00 mmol) were sequentially added to the resulting suspension. The mixture was stirred for an additional 30 min at ambient temperature, 1 M hydrochloric acid (10 mL) was added. The products were extracted with hexane/ethyl acetate (5:1, 10 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. Silica gel column purification (hexane/ethyl acetate = 10:1) gave homoallyl alcohol **2a** (0.152 g, 0.94 mmol, *erythro*/*threo* = 48:52) in 94% yield.

4.3. Preparation of erythro- and threo-*1f*

Under an atmosphere of argon, 2,4,6-trimethylbenzaldehyde (2.96 g, 20.0 mmol) was added dropwise to methylmagnesium bromide (1.17 M THF solution, 20.5 mL, 24.0 mmol) in 30 mL of ether at 0 °C in a 100-mL reaction flask. After being stirred for 2 h at 25 °C, the mixture was poured into 1 M hydrochloric acid (30 mL). The products were extracted with ether (30 mL × 3). The organic layer was dried over $MgSO_4$, and solvent was removed under reduced pressure. Chromatographic purification on silica gel (hexane/ethyl acetate = 5:1) afforded 2.96 g of 1-mesitylethanol (18.3 mmol) in 91% yield as a white solid.

Pyridinium chlorochromate (5.82 g, 27 mmol) and silica gel (Wako Pure Chemical C-200, 5.82 g) were ground in a mortar. The resulting orange powder was transferred to a 100-mL reaction flask. Dichloromethane (50 mL) and 1-mesitylethanol (2.96 g, 18.3 mmol) were added with swirling under argon at 0 °C. The mixture turned black and was stirred for 12 h at room temperature. The mixture was diluted with ether (30 mL) and filtered through a pad of Celite. The filtrate was evaporated in vacuo. Silica gel column purification (hexane/ethyl acetate = 5:1) provided mesityl methyl ketone (2.43 g, 15.3 mmol, 85% yield) as a colorless oil.

Diethyl ether (40 mL) and crotylmagnesium chloride (0.95 M THF solution, 17.4 mL, 16.5 mmol) were added to a 100-mL reaction flask under argon. At 0 °C, the ketone (2.43 g, 15.3 mmol) was added dropwise to the solution. After being stirred for 2 h at room temperature, the mixture was poured into 30 mL of 1 M HCl. The products were extracted with ether three times (30 mL each). Concentration left a colorless oil. Silica gel column purification with toluene as an eluent twice allowed complete separation of *erythro*-**1f** (1.80 g, 8.26 mmol, 54%, faster moving band, $R_f = 0.31$, toluene) and *threo*-**1f** (0.77 g, 3.52 g, 23%, slower moving band, $R_f = 0.24$, toluene).

4.4. Stereoselective crotylation from diastereomerically pure *1f* (Scheme 2)

Carbinol *erythro*-**1f** (0.262 g, 1.20 mmol) was dissolved in ether (10 mL) under argon. Methylmagnesium iodide (1.0 M, 1.20 mL. 1.2 mmol) in ether was added to the solution at −20 °C, and the resulting mixture was stirred for 1 h. At the same temperature, gallium trichloride (1.0 M hexane solution, 1.20 mL, 1.2 mmol) and benzaldehyde (0.11 g, 1.0 mmol) were added. After the mixture was stirred at −20 °C for 17 h, the reaction was quenched with 1 M hydrochloric acid at −20 °C. The mixture was allowed to warm to ambient temperature and was stirred for 10 min. Extraction, evaporation, and purification on silica gel (hexane/ethyl acetate = 10:1) furnished **2a** (0.152 g, 0.94 mmol, 94% yield) as a 96:4 mixture of *erythro* and *threo* isomers.

4.5. Stereochemical assignment of erythro-*1f*

THF (5.0 mL) was placed in a 30-mL reaction flask under argon. The oil of **1f** (109 mg, 0.50 mmol), which was the faster moving band of $R_f = 0.31$ (toluene), was dissolved in THF (1.5 mL), and the solution was added to the reaction flask. 9-Borabicyclo[3.3.1]nonane (9-BBN, 0.183 g, 1.5 mmol) in THF (1.5 mL) was added at ambient temperature. After the mixture was stirred for 3 h, water (0.30 mL), 6 M NaOH (0.25 mL, 1.5 mmol), and 30% hydrogen peroxide (0.50 mL, 4.5 mmol) were sequentially added. A slightly exothermic reaction took place. The reaction was quenched with aqueous sodium thiosulfate, and the products were extracted with ethyl acetate. After removal of solvent, silica gel column purification yielded 0.043 g of 3-methyl-4-(2,4,6-trimethylphenyl)-1,4-pentanediol (0.18 mmol, 36% yield, unoptimized). X-ray quality crystals were grown from pentane/dichloromethane (Fig. 1). Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC 265711). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: 44-1223-3360033 or e-mail: deposit@ccdc.cam.ac.uk.

4.6. Allylgallation of alkynes (Table 4)

Homoallyl alcohol **1a** (0.170 g, 1.00 mmol) and dioxane (5 mL) were placed in a 20-mL two-necked reaction flask equipped with a Dimroth condenser. Methylmagnesium iodide (1.0 M ethereal solution, 1.0 mL, 1.0 mmol) was then added to the reaction flask at ambient temperature. After the reaction mixture was stirred for 1 h, a hexane solution of gallium trichloride (1.0 M, 1.0 mL. 1.0 mmol) was added to the resulting suspension. Alkyne **5a** (66 mg, 0.50 mmol) in dioxane (1.0 mL) was added. The mixture was heated at reflux for 2 h. After cooling, the reaction was quenched with 10 mL of 1 M hydrochloric acid. The product was extracted with hexane/ethyl acetate (10:1, 10 mL each, three times). The combined organic layer was dried over sodium sulfate. Evaporation under a reduced pressure yielded an oil. Silica gel column chromatography of the oil (hexane/ethyl acetate = 40:1) provided 90.3 mg of **6a** (0.48 mmol, 96% yield) as a colorless oil.

4.7. Characterization data

The following compounds were characterized according to the literature: **2a** [11], **2b** [12], **2c** [11], **2d** [11], **2e** [13], **2f** [11], **2h** [14], **2i** [15], **2j** [15], **2k**–**m** [11], **2n** [16], **2o** [14], **2p** [17], **2q** [17], **6b** [18], **6f** [18], **6g** [18], **6g-d_2** [19], **6g-d_1** [20], **6i** [18], and **6n** [21].

4.7.1. (E)-3-Methyl-1,5-tetradecadien-4-ol (2 g, mixture of diastereomers)

IR (neat) 3355, 2925, 2855, 1640, 1456, 1372, 1250, 969, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.0$ Hz, 3H), 0.98 (d, $J = 7.0$ Hz, $0.48 \times 3H$), 1.01 (d, $J = 7.0$ Hz, $0.52 \times 3H$), 1.26 (m, 10H), 1.36 (m, 2H), 1.60 (br s, 1H), 2.09 (m, 2H), 2.22 (m, $J = 7.0$ Hz, $0.48 \times 1H$), 2.36 (m, $J = 7.0$ Hz, $0.52 \times 1H$), 3.79 (t, $J = 7.0$ Hz, $0.48 \times 1H$), 3.96 (t, $J = 7.0$ Hz, $0.52 \times 1H$), 5.07–5.16 (m, 2H), 5.39–5.46 (m, 1H), 5.61–5.69 (m, 1H), 5.82–5.70 (m, 1H); ^{13}C NMR ($CDCl_3$, some signals overlap) δ 14.34, 15.09, 16.39, 22.89, 29.35, 29.38, 29.40, 29.50, 29.65, 32.10, 32.51, 43.88, 44.83, 76.21, 76.54, 115.86, 116.59, 130.21, 130.63, 133.57. 134.24, 140.36, 140.87; Anal. Calc. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.54; H, 12.75%.

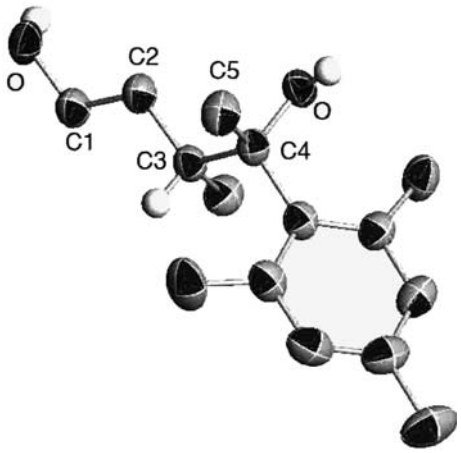


Fig. 1. ORTEP diagram of *erythro*-3-methyl-4-(2,4,6-trimethylphenyl)-1,4-pentanediol. Some hydrogen atoms are omitted for clarity.

4.7.2. 2-(4-Methoxyphenyl)-3-methyl-1,4-pentadiene (6a)

IR (neat) 2835, 1609, 1512, 1246, 1180, 1036, 999, 897, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, $J = 6.5$ Hz, 3H), 3.35–3.41 (m, 1H), 3.81 (s, 3H), 5.00–5.08 (m, 3H), 5.21 (d, $J = 1.5$ Hz, 1H), 5.91 (ddd, $J = 17.0$, 10.5, 7.0 Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.33 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.47, 41.97, 55.46, 111.03, 113.69, 113.80, 127.89, 134.75, 142.75, 152.08, 159.09; Anal. Calc. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.70; H, 8.60%.

4.7.3. 2-(4-Fluorophenyl)-3-methyl-1,4-pentadiene (6c)

IR (neat) 3085, 2972, 2934, 2876, 1627, 1604, 1509, 1456, 1232, 1160, 1015, 913, 840, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, $J = 7.0$ Hz, 3H), 3.33–3.39 (m, 1H), 5.03 (dm, $J = 10.5$ Hz, 1H), 5.06 (dm, $J = 17.0$ Hz, 1H), 5.08 (d, $J = 1.0$ Hz, 1H), 5.22 (d, $J = 1.0$ Hz, 1H), 5.89 (ddd, $J = 17.0$, 10.5, 7.0 Hz, 1H), 6.98–7.03 (m, 2H), 7.32–7.36 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.37, 42.22, 112.43, 114.11, 115.13 (d, $J = 21.1$ Hz), 128.43 (d, $J = 7.7$ Hz), 138.35 (d, $J = 2.9$ Hz), 142.37, 151.76, 162.35 (d, $J = 245.8$ Hz); ^{19}F NMR ($CDCl_3$) δ −115.90; Anal. Calc. for $C_{12}H_{13}F$: C, 81.78; H, 7.44. Found: C, 81.51; H, 7.46%.

4.7.4. 2-[4-(N,N-Dimethylamino)phenyl]-3-methyl-1,4-pentadiene (6d)

IR (neat) 3082, 2968, 2930, 2880, 2800, 1611, 1522, 1445, 1354, 1227, 1202, 1169, 910, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (d, $J = 6.5$ Hz, 3H), 2.96 (s, 6H), 3.41 (quintet of doublet, $J = 6.5$, 1.5 Hz, 1H), 4.94 (s, 1H), 5.01 (dt, $J = 10.5$, 1.5 Hz, 1H), 5.07 (dt, $J = 17.0$, 1.5 Hz, 1H), 5.21 (d, $J = 1.5$ Hz, 1H), 5.95 (ddd, $J = 16.5$, 10.0, 6.5 Hz, 1H), 6.70 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.57, 40.77, 41.59, 109.33, 112.33, 113.50, 127.43, 130.17, 143.12, 150.07, 152.16; Anal. Calc. for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.78; H, 9.58%.

4.7.5. 2-Decyl-3-methyl-1,4-pentadiene (6e)

IR (neat) 3404, 3082, 2961, 2926, 2855, 1636, 1466, 910, 893 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.0$ Hz, 3H), 1.13 (d, $J = 6.5$ Hz, 3H), 1.20 (br s, 14H), 1.42 (m, 2H), 2.00 (t, $J = 7.5$ Hz, 2H), 2.79 (quintet of doublet 7.0, 1.0 Hz, 1H), 4.75 (q, $J = 1.5$ Hz, 1H), 4.77 (br s, 1H), 4.97 (ddd, $J = 10.5$, 1.5, 1.0 Hz, 1H), 5.01 (dt, $J = 17.5$, 1.5 Hz, 1H), 5.76 (ddd, $J = 17.5$, 10.0, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.35, 18.98, 22.92, 28.20, 29.57, 29.73, 29.81, 29.86 (×2), 32.14, 34.74, 43.79, 108.16, 113.32, 143.18, 153.50; Anal. Calc. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.19; H, 13.31%.

*4.7.6. 2-(4-Methylphenyl)-4-methyl-1,4-pentadiene (**6h**)*

IR (neat) 2968, 2936, 2910, 2835, 1609, 1512, 1440, 1288, 1248, 1180, 1036, 891, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (s, 3H), 3.19 (s, 2H), 3.81 (s, 3H), 4.76 (m, 1H), 4.81 (m, 1H), 5.03 (dd, $J = 2.5$, 1.5 Hz, 1H), 5.36 (d, $J = 1.5$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.38 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.51, 44.32, 55.45, 112.62, 112.93, 113.72, 127.40, 133.59, 143.87, 145.07, 159.20; Anal. Calc. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.67; H, 8.48%.

*4.7.7. 2-(4-Fluorophenyl)-4-methyl-1,4-pentadiene (**6j**)*

IR (neat) 3080, 2972, 2914, 1651, 1626, 1602, 1510, 1443, 1375, 1234, 1161, 895, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (s, 3H), 3.20 (s, 2H), 4.76 (br s, 1H), 4.82 (br s, 1H), 5.11 (d, $J = 1.5$ Hz, 1H), 5.39 (d, $J = 1.5$ Hz, 1H), 7.00 (dd, $J = 9.0$, 9.0 Hz, 2H), 7.40 (dd, $J = 9.0$, 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.45, 44.41, 112.87, 114.48, 115.18 (d, $J = 21.5$ Hz), 127.91 (d, $J = 8.2$ Hz), 137.18, 143.48, 144.82, 162.44 (d, $J = 246.4$ Hz); Anal. Calc. for $C_{12}H_{13}F$: C, 81.78; H, 7.44. Found: C, 81.69; H, 7.68%.

*4.7.8. 2-[4-(N,N-Dimethylamino)phenyl]-4-methyl-1,4-pentadiene (**6k**)*

IR (neat) 3078, 3042, 2968, 2912, 2853, 2800, 1611, 1524, 1445, 1354, 818 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (s, 3H), 2.95 (s, 6H), 3.19 (s, 2H), 4.78 (m, 1H), 4.81 (m, 1H), 4.95 (d, $J = 1.5$ Hz, 1H), 5.34 (d, $J = 1.5$ Hz, 1H), 6.68 (d, $J = 9.0$ Hz, 2H), 7.36 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.56, 40.73, 44.18, 111.08, 112.26, 112.38, 127.00, 129.04, 144.23, 145.11, 150.12; Anal. Calc. for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.74; H, 9.63%.

*4.7.9. 2-Decyl-4-methyl-1,4-pentadiene (**6l**)*

IR (neat) 3406, 3387, 3074, 2957, 2926, 2855, 1639, 1466, 1439, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.0$ Hz, 3H), 1.26 (br s, 14H), 1.41 (m, 2H), 1.67 (m, 3H), 1.96 (t, $J = 7.5$ Hz, 2H), 2.72 (s, 2H), 4.73 (m, 1H), 4.76 (m, 1H), 4.79 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.35, 22.04, 22.92, 27.87, 29.58, 29.63, 29.78, 29.86 (×2), 32.14, 35.42, 45.70, 110.93, 112.25, 144.03, 147.82; Anal. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.13; H, 13.38%.

*4.7.10. 3,3-Dimethyl-2-(4-methoxyphenyl)-1,4-pentadiene (**6m**)*

IR (neat) 3085, 2930, 2835, 1609, 1511, 1464, 1442, 1413, 1375, 1287, 1245, 1175, 1038, 910, 834 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 6H), 3.80 (s, 3H), 4.91 (d, $J = 1.5$ Hz, 1H), 5.01 (dd, $J = 17.0$, 1.0 Hz, 1H), 5.02 (dd, $J = 11.0$, 1.0 Hz, 1H), 5.18 (d, $J = 1.5$ Hz, 1H), 5.97 (dd, $J = 17.0$, 11.0 Hz, 1H), 6.80 (d, $J = 9.0$ Hz, 2H), 7.14 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 27.19, 42.65, 55.38, 111.51, 112.86, 113.33, 130.05, 135.60, 147.62, 156.83, 158.46; Anal. Calc. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.82; H, 9.05%.

Acknowledgements

This work is supported by Grant-in-Aid for Scientific Research on Priority Areas, Reaction Control of Dynamic Complexes, from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. K.H. thanks JSPS for financial support. We thank Professor Masaki Shimizu (Kyoto University) for helping with the X-ray crystallographic analysis.

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