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Direct Construction of Quaternary Carbons from Carbonyl Compounds Utilizing Low-Valent Vanadium Complexes

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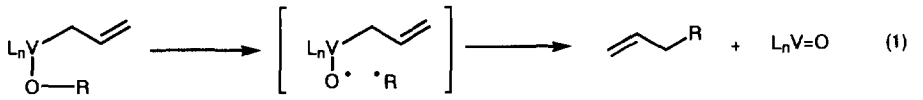
Abstract: Direct geminal diallylation of a carbonyl compound with allyl bromide has been achieved in the presence of a low-valent vanadium complex and zinc. The diallylation has been found to proceed stepwise and the two allyl groups were introduced successively. By applying this method, one-pot synthesis of asymmetric quaternary carbons has been accomplished. As the first alkylating reagent a combination of allyl bromide and zinc, a Grignard reagent, or an alkyllithium can be used. The second one should be the combination of a low-valent vanadium(II) complex and allyl bromide, benzyl bromide, or propargyl bromide. Strong oxophilicity of the low-valent vanadium facilitated the deoxygenative allylation. © 1997 Elsevier Science Ltd.

INTRODUCTION

Development of new methodology for formation of C-C bonds utilizing so far unknown specific reactivity of metal complexes draws much attention in synthetic organic chemistry.[1] In particular, discovery of new synthetic methods with high selectivities induced by early transition metal reagents has become of interest in recent years.[1b] Although several methods for the synthesis of quaternary carbons have been reported,[2] direct transformation from carbonyl compounds, which is one of the most attractive synthetic strategy,[3] was confined to the geminal dimethylation mediated by Me_2TiCl_2[4] or Me_3Al[5] but an extension of these methods to general alkylation failed.[4e] Thus, development of new efficient and general methods of replacement of the oxygen atom in carbonyl compounds by two kinds of alkyl groups are desired.

Vanadium(II) complexes have been recognized to be highly capable of one-electron reduction, thereby inducing radical reactions such as reduction of several organic substrates[6] and pinacol-type reductive coupling.[7] Besides these radical reactions, however, there seems to be no examples of C-C bond forming reactions promoted by vanadium(II) species. For example, in an attempted allylation of ketones using allyl halide and vanadium(II) species,[8,9] the reductive dimerization of allyl halide induced by the homolytic cleavage of the V-C bond of the allylvanadium species was so fast that the allylation of carbonyl compounds scarcely proceeded.[6h] In order to design a successful allylation using vanadium(II) and allyl halides, this disadvantage must be overcome. We have already reported that by employing HMPA (HMPA = hexamethylphosphoric triamide) as a co-solvent, generation of radical species was suppressed.[10] Another strategy to solve the problem is the capture of the radical species by the allyl group. The important point of this strategy is to prevent the homocoupling of

the radical species, so that we have designed an intramolecular reaction in which the generation and the capture of a radical species take place within the same vanadium complex. If an alkoxy(allyl)vanadium species was produced in the reaction mixture, the high oxophilicity of the vanadium complex could make it possible for the vanadium to pick up the oxygen from the C-O single bond[11] generating a new radical species. The radical species thus formed could be captured by the allyl group on the same vanadium metal before the homocoupling takes place, as shown in eq 1.

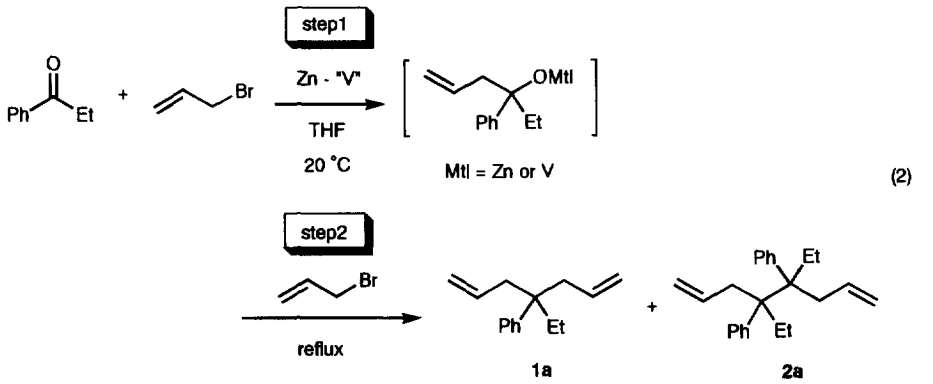


(1)

We report herein deoxygenative allylation from alkoxy(allyl)vanadium species derived from allyl halides and an alkoxyvanadium(II) species and its application to direct construction of asymmetric quaternary carbons from ketones.[12]

RESULTS AND DISCUSSION

Geminal Diallylation of Propiophenone. The reaction of propiophenone and allyl bromide in the presence of $VCl_2(tmeda)_2$[13] [tmeda = *N*, *N*, *N'*, *N'*-tetramethylethylenediamine] at 20 °C in THF afforded the allylation product of propiophenone, 3-phenylhex-5-en-3-ol, though in a low yield (19%).[10] When the reaction mixture was heated under reflux with excess amount of allyl bromide, the deoxygenative diallylation product was obtained in a similar yield instead of the homoallyl alcohol. Namely, when a mixture of propiophenone (1.0 equiv, 2.5 x 10^{-2} mol/L) and allyl bromide (4.0 equiv) was stirred in THF in the presence of $VCl_2(tmeda)_2$ (4.0 equiv) at 20 °C for 20 h (step 1) and then the resulting reaction mixture was heated under reflux for 12 h (step 2), a diallyl compound, 4-ethyl-4-phenylhepta-1,6-diene (**1a**) was isolated in 18% yield. The remaining propiophenone was recovered unchanged after hydrolysis of the reaction mixture and no other product was detected except hexa-1,5-diene, a reductive coupling product of excess allyl bromide. Both step 1 (the reaction at 20 °C for 20 h) and step 2 (the reaction under reflux in the presence of one more equivalent of allyl bromide) are indispensable for the diallylation (eq 2).



(2)

Without step 1 the starting ketone was recovered unchanged, presumably due to the predominant formation of hexa-1,5-diene. Without step 2 only the homoallyl alcohol, 3-phenylhex-5-en-3-ol (**3**), the hydrolyzed product of the intermediate metal alkoxide, was obtained in 19% yield. The yield of the alcohol **3** was comparable with that of **1a** obtained after step 2 had been carried out. Before the heating (step 2), formation of the homoallyl alcohol, a hydrolyzed product of a homoallyloxyvanadium species, was detected by TLC. As the reaction proceeded, the yield of the diallyl compound increased gradually with decreasing the amount of the homoallyl alcohol. These observations suggested that the alkoxyvanadium species formed initially and then reacted with allyl bromide under reflux conditions in THF to give the diallyl compound. These results prompted us to search for a suitable reaction condition for the deoxygenative diallylation of ketones. Several representative results are summarized in Table 1.

Table 1. Direct Geminal Diallylation of Propiophenone[a]

run	Reagent (Zn - V)	time (h)[b]		yield (%)[c]		recovery of propiophenone (%)
		step 1	step 2	**1a**	**2a**[d]	
1	$VCl_2(tmeda)_2$	20	12	18	0	72
2	$[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$	20	12	0	0	100
3	$VCl_2(tmeda)_2$ + Zn[e]	0.5	12	59	33	0
4	$VCl_3(thf)_3$ + Zn[f]	0.5	12	64	14	0
5	$VCl_2(tmeda)_2$ + Zn[e,g]	0.5	12	84	15	0

[a] Propiophenone (1.0 equiv), allyl bromide (4.0 equiv), and a vanadium(II) reagent (4.0 equiv) were employed in THF. [b] step 1 : 20°C, step 2 : reflux. [c] Isolated yield. [d] *dl* : *meso* ≈ 1 : 1. [e] Two equivalents of zinc were used. [f] Four equivalents of zinc were used. [g] High dilution condition; the reaction mixture was diluted to 10 times with THF and 2.0 equiv of allyl bromide were added, see Experimental Section.

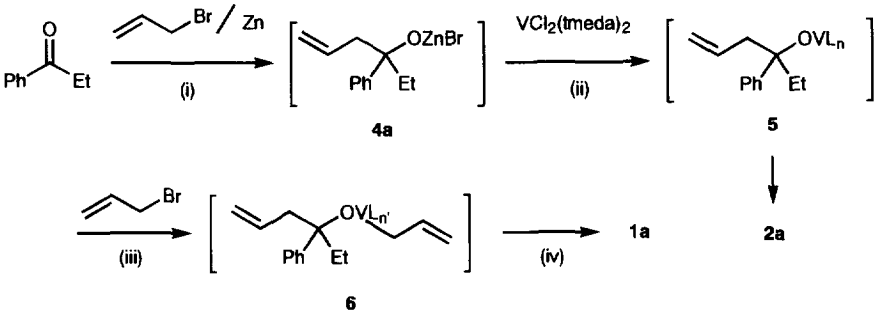
When another vanadium(II) reagent, $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, prepared in advance and purified,[14] which was more effective for the monoallylation of carbonyl compounds in the presence of HMPA than $VCl_2(tmeda)_2$,[10] was used, neither geminal diallylation nor monoallylation of propiophenone occurred (run 2). Inefficiency of the binuclear complex salt is partly considered to be due to its low solubility. If $VCl_2(tmeda)_2$ was employed together with two equivalents of zinc, the pretreatment time of the step 1 can be shortened to 0.5 h and the yield of **1a** increased to 59% but the deoxyhomocoupling product from an intermediate, homoallyloxyvanadium species, 4,5-diethyl-4,5-diphenylocta-1,7-diene (**2a**) (*dl* : *meso* ≈ 1 : 1) also formed in a substantial amount (run 3). A similar result was also achieved by employing a divalent vanadium species, $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$, generated *in situ* from $VCl_3(thf)_3$ and excess zinc (run 4). By employing a high dilution technique (the concentration of propiophenone was reduced to 2.5 x 10^{-3} mol/L, see Experimental Section) in step 2 of run 3, the yield of **1a** was greatly improved to 84% and the formation of **2a** was

suppressed to 15% (run 5). An increase in the yield of **8** was also achieved with a $VCl_3(thf)_3$ + Zn system under a high dilution condition, though the yield of **2a** remained in a similar level to that of run 4. If the vanadium compounds were not present in these vanadium-zinc system, only homoallyl alcohol **3** was produced quantitatively under similar conditions.

The present geminal diallylation of propiophenone is characteristic of vanadium(II) species. When a vanadium(III) or a vanadium(IV) species, $VCl_3(thf)_3$ or VCl_4, was used, the geminal diallylation product **1a** was obtained in only a very low yield. The other early transition metal complexes such as $TiCl_4$, $ZrCl_4$, $NbCl_5$, $TaCl_5$, $CrCl_3(thf)_3$, etc., in combination with zinc did not promote a similar diallylation of ketone.[15]

Mechanism of the Diallylation. On the basis of the above observations a plausible mechanism is shown in Scheme 1. Present diallylation of propiophenone involves 4 steps; (i) a monoallylation of propiophenone mediated by allyl bromide and zinc to form a homoallyloxyzinc species **4a**, (ii) transmetallation between the zinc alkoxide and $VCl_2(tmeda)_2$ to form an alkoxy(allyl)vanadium(II) species **5**, (iii) oxidative addition of allyl bromide to **5** formed an alkoxyvanadium(IV) species **6**, and then finally (iv) elimination of oxovanadium species from **6** giving the diallyl compound **1a**. The homocoupling product **2a** was obtained by radical coupling of alkoxyvanadium **5**.

Scheme 1 A Plausible Mechanism



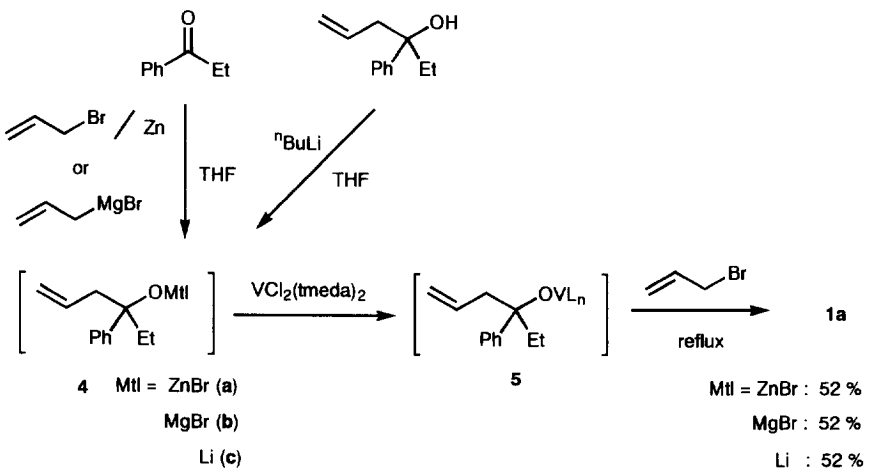
The improvement of the yield of the diallylation product **1a** in this reaction by the high dilution technique may indicate that the rate determining step for the introduction of the second allyl group proceeds via an *intramolecular* reaction and the homocoupling product was obtained by an *intermolecular* radical coupling reaction. Thus, both the alkoxy group and the allyl group coordinated to the same vanadium metal such as **6** and the intramolecular allylation accompanying C-O bond cleavage occurred. Strong oxophilicity of the vanadium facilitated the deoxygenative diallylation.[16]

In order to get further mechanistic information about the geminal diallylation, at first we have prepared a homoallyloxyvanadium species **5** in advance via transmetallation and then made it react with allyl bromide (Scheme 2). To the zinc alkoxide **4a** (Mtl = Zn) generated from propiophenone (1.0 equiv), allyl bromide (1.1 equiv), and zinc (1.1 equiv) in THF was added a blue THF solution of $VCl_2(tmeda)_2$ (2.0 equiv). During being stirred at 20 °C for 1 h, the color of the reaction mixture changed from blue to dark green. To the resulting dark green solution of the vanadium alkoxide was added an excess of allyl bromide (4.0 equiv) and the whole mixture was refluxed for 15 h to give the diallyl compound **1a** in 52% yield along with the coupling

product **2a** in 33% yield; the result is very similar to those obtained for the direct diallylation of propiophenone by allyl bromide using a $VCl_2(tmeda)_2$-Zn or a $VCl_3(thf)_3$-Zn system (run 3 and 4 in Table 1). The deoxygenative C-C coupling of the zinc alkoxide with allyl bromide did not proceed in the absence of $VCl_2(tmeda)_2$ under similar conditions and neither the diallyl compound **1a** nor the coupling product **2a** was produced. Change of the color of the reaction mixture and indispensability of a low-valent vanadium(II) species for formation of **1a** and **2a** suggested strongly that the alkoxyvanadium complex **5** formed at first through transmetallation between the initially formed zinc alkoxide and $VCl_2(tmeda)_2$ and then reacted with allyl bromide to give **1a** and **2a**.[17] Before being worked up, the reaction mixture was concentrated *in vacuo* to afford a black residue. An IR spectrum of the residue showed a sharp V=O stretching at 965 cm^{-1}, which indicates that the oxygen was removed from an alkoxyvanadium species as an oxovanadium species.[18]

In this vanadium(II) mediated diallylation, even if the magnesium alkoxide **4b** (Mtl = MgBr) or the lithium alkoxide **4c** (Mtl = Li) instead of the zinc alkoxide **4a** was used as an initial alkoxide, the diallyl compound **1a** and the coupling product **2a** were obtained in similar yields; the magnesium alkoxide gave 52% of **1a** and 40% of **2a** and the lithium alkoxide gave 52% of **1a** and 47% of **2a**.

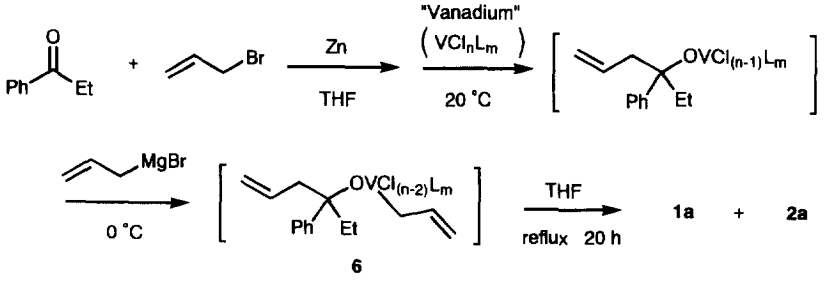
Scheme 2



Next, we prepared *in situ* several alkoxy(allyl)vanadium species **6** having various oxidation states and examined the effect of the valency of the vanadium on the deoxygenative allylation (Scheme 3). The alkoxy(allyl)vanadium complexes **6** were generated *in situ* from several vanadium chloride complexes having a different kind of oxidation state by transmetallation with one equiv of alkoxyzinc and by the subsequent reaction with one equiv of an allyl Grignard reagent in THF at 0 °C. The THF solution of the complex **6** thus obtained was then refluxed for 20 h. When a divalent vanadium complex, $VCl_2(tmeda)_2$, or a trivalent vanadium complex, $VCl_3(thf)_3$, was employed, the elimination of the oxovanadium species from the resulting alkoxy(allyl)vanadium species **6** did scarcely proceed and the main product was the homoallyl alcohol **3**. When a tetravalent vanadium complex, VCl_4-TMEDA, was employed, however, the diallyl compound **1a** was isolated in 10% yield along with the coupling product **2a** in 50% yield. These observations suggest that the

elimination of the oxovanadium species can only proceed from the alkoxy(allyl)vanadium(IV) species **6**. In the step (iii) in Scheme 1, oxidative addition of an allyl bromide to the vanadium(II) alkoxide should form an allyl(homoallyloxy)vanadium(IV) species **6**, from which elimination of a "V=O" species proceeded to afford the diallyl product.

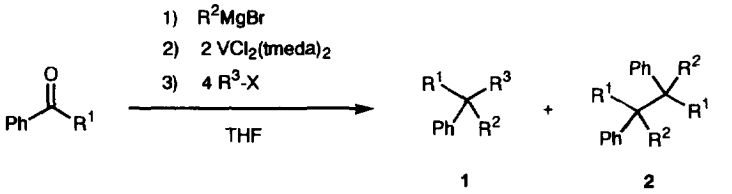
Scheme 3

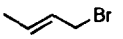
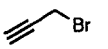


	"Vanadium"	1a	2a
(i)	$VCl_2(tmeda)_2$	0 %	trace
(ii)	$VCl_3(thf)_3$	0 %	< 20 %
(iii)	VCl_4 / TMEDA	10 %	50 %

Preparation of Asymmetric Quaternary Carbon Compounds. This transmetallation technique afforded also a novel method of general construction of asymmetric quaternary carbons from carbonyl compounds. The results are shown in Table 2. For example, propiophenone was first reacted with methylmagnesium bromide (1.0 equiv) in THF and then treated with $VCl_2(tmeda)_2$ (2.0 equiv) at 20 °C for 1 h. The reaction mixture was finally heated under reflux in the presence of allyl bromide (4.0 equiv) to give an asymmetric quaternary compound, an allyl methyl compound **1b**, in 50% yield along with the homocoupling product **2b** in 46% yield (run 1 in Table 2). When the reaction was carried out under dilution conditions (*vide infra*), the yield of **1b** also increased to 60% yield and that of **2b** decreased to 39% (run 2). The increase in the yield of **1** under the high dilution conditions was observed in every case. Ethyl Grignard reagent can also be employed to give an asymmetric quaternary carbon compound **1c** in a moderate yield (run 3). When crotyl bromide was used as the second alkylating reagent, a quaternary carbon product **1d** was obtained in 74% isolated yield under high dilution conditions (run 6), as a mixture of the regio- and the stereoisomers (the ratio of the regio isomers, major : minor = 54 : 46). In the monoallylation of a carbonyl compound using crotyl bromide mediated by vanadium(II) complexes in a mixed solvent of THF and HMPA, the γ-product was selectively obtained.[10] These results indicate that the second deoxyalkylation step in this reaction proceeds by a radical mechanism and not nucleophilic attack of the allylvanadium species. Although propargyl bromide and benzyl bromide can also be used as the second alkylating reagent and gave the quaternary carbon products **1f** and **1e** respectively in moderate yields, MeI and PhI were not effective. Probably the oxidative addition of MeI or PhI to a vanadium(II) complexes did not proceed efficiently. When benzaldehyde was employed as a

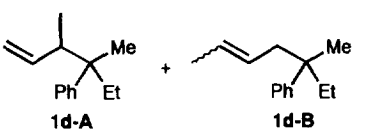
Table 2. General Constraction of Asymmetric Quaternary Carbons[a]



run	R^1	R^2		R^3-X	yield (%)[b] 1	yield (%)[b] 2[c]
1	Et	Me	(b)		50	46
2[d]	Et	Me	(b)	〃	60	39
3	Et	Et	(c)	〃	50	26
4	Et	Allyl	(a)	〃	52	40
5	Et	Me	(d)		41[e]	43
6[d]	Et	Me	(d)	〃	74[e]	22
7	Et	Me	(e)	$PhCH_2Br$	32	45
8[d]	Et	Me	(e)	〃	63	23
9	Et	Me	(f)		21[f]	49
10[d]	Et	Me	(f)	〃	43[f]	30
11	Me	Et	(b)		44	42
12	Ph	Ph	(g)	〃	72	9
13	H	Ph	(h)	〃	50	35
14	Et	Me		MeI	0	0
15	Et	Me		PhI	0	0

[a] Carbonyl compounds (1.0 equiv, 3 x 10^{-2} mol/L), Grignard reagents (1.0 equiv), $VCl_2(tmeda)_2$ (2.0 equiv), and alkyl halides (4.0 equiv) were employed in THF. [b] Isolated yield. [c] *dl* : *meso* ≈ 1 : 1. [d] The reaction mixture was diluted, 2 x 10^{-3} mol/L.

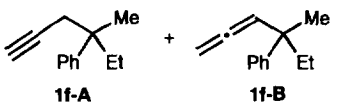
[e] A mixture of regio- and stereoisomers.



1d-A **1d-B**

Run 5; A : B = 61 : 39
Run 6; A : B = 54 : 46

[f] A mixture of isomers.

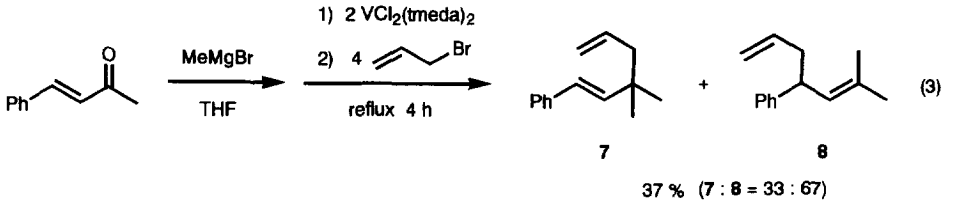


1f-A **1f-B**

Run 9; A : B = 48 : 52
Run 10; A : B = 63 : 37

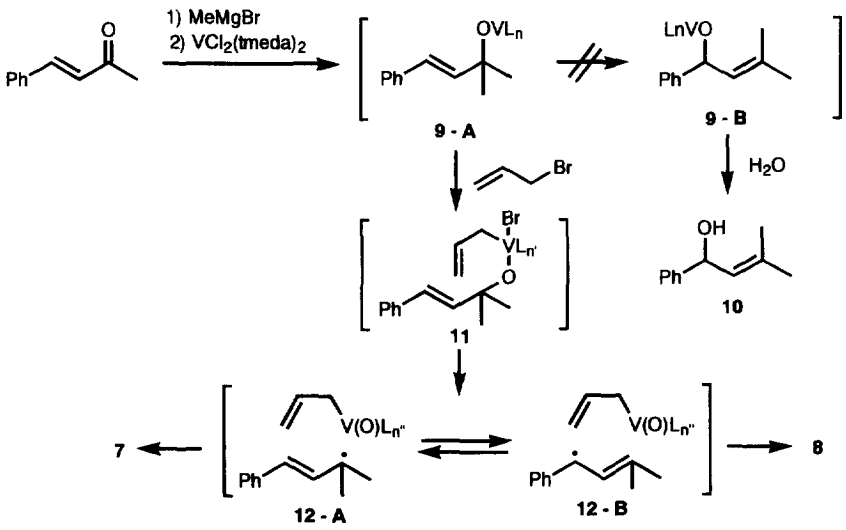
starting carbonyl compound, the C-O bond cleavage did not occur except the case in combination with PhMgBr (run 13).

Deoxygenative Alkyl Allylation of α,β-Unsaturated Carbonyl Compounds. When benzalacetone, as an α,β-unsaturated ketone, reacted with MeMgBr and allyl bromide in the presence of $VCl_2(tmeda)_2$, the C-O bond cleavage of the alkoxyvanadium species occurred to produce the deoxyallylation products as a mixture of regioisomers (**7** : **8** = 33 : 67) in 37% yield along with the homocoupling products of benzalacetone in 35% yield (eq 3). One is a quaternary carbon product **7** and the other is a tertiary carbon product **8**. In **8** an allyl group was introduced at the α-position of the phenyl group (the β-carbon of the original carbonyl group). Rearrangement from **7** to **8** might be negligible under these conditions since the ratio of the regioisomers did not change after a prolonged reaction time (19 h, 39%, **7** : **8** = 36 : 64) and at high reaction temperature (in DMF, 15 h, 41%, **7** : **8** = 34 : 66).



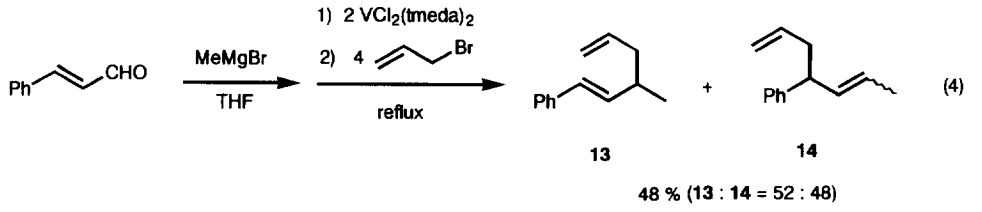
A plausible reaction pathway to give the deoxygenative allylation products **7** and **8** is depicted in Scheme 4. The alkoxyvanadium species **9-A** should be produced via transmetallation from a magnesium alkoxide to vanadium. Since the allyl alcohol **10** derived from vanadium alkoxide **9-B** was not detected at all during this reaction, there should not be present the isomerization from the allyloxyvanadium **9-A** to **9-B**. Thus, **9-A** should have reacted with allyl bromide as the second alkylating reagent to afford the key intermediate **11**, from which an oxovanadium species was eliminated to produce a mixture of **7** and **8** presumably via radical inter-

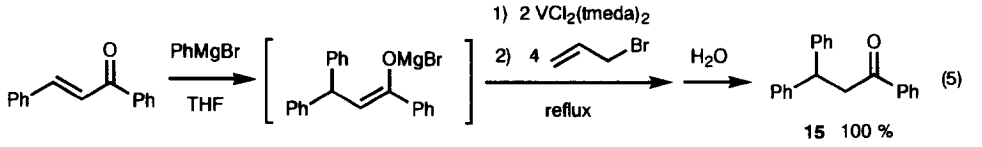
Scheme 4



mediates **12**. The equilibrium between **12-A** and **12-B** would be so fast compared to the intramolecular coupling reaction of allyl groups. The ratio of **7** and **8** should depend upon the stability of these radical species **12**.

Although the deoxygenated product was not obtained from aldehyde by the present deoxygenative allylation except the case, the combination of benzaldehyde and PhMgBr (run 13 in Table 2), the deoxygenative reaction from α,β–unsaturated aldehyde proceeded to give two kinds of regioisomers, **13** and **14**, similarly to the case from α,β–unsaturated ketone (eq 4). On the contrary, elimination of an oxovanadium species from a vanadium enolate did not proceed at all. Reaction of a magnesium enolate, derived from 1,4-addition of PhMgBr to benzalacetophenone in THF, with allyl bromide in the presence of $VCl_2(tmeda)_2$ afforded only β,β-diphenyl propiophenone **15** quantitatively after hydrolysis of the reaction mixtures and the deoxyallylation product was not obtained (eq 5).





In summary, asymmetric quaternary carbons were synthesized directly from carbonyl compounds by using high oxophilicity and strong reducing power of vanadium(II) complexes. In this reaction two kind of alkyl groups were introduced stepwise to a carbonyl carbon. At the first step, any alkylating reagent such as Grignard reagent, alkyl lithium or alkyl zinc reagents can be used. On the other hand, at the second step, an allyl, a benzyl or a propargyl group can be introduced.

EXPERIMENTAL SECTION

All manipulations were conducted under argon atmosphere with standard Schlenk methods. Unless otherwise noted, carbonyl compounds and alkyl halides were obtained from commercial suppliers and were used after distillation. THF was distilled from sodium benzophenone ketyl under argon prior to use. DMF and TMEDA are distilled from calcium hydride under argon prior to use. $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$,[14] $VCl_2(tmeda)_2$,[13] and $VCl_3(thf)_3$[19] were prepared according to the published procedures. VCl_4 was obtained from a commercial supplier (Aldrich) and was used as received. Column chromatography was conducted by using silica gel 60 (E. Merck 9385 230-400 mesh). The melting points were recorded on a Yanaco MP-52982

and were uncorrected. IR spectra were determined with a Hitachi 295 spectrophotometer or a JASCO FT/IR-230. Mass spectra were obtained on a JEOL JMS DX-303HF spectrometer. ^{1}H NMR spectra were recorded at 270.05 MHz on a JEOL GSX-270 spectrometer. Chemical shifts of ^{1}H NMR are expressed in ppm downfield from Me_4Si using δ scale ($CHCl_3$ was used as an internal standard, δ 7.26). Elemental analyses were carried out with a Perkin Elmer 2400.

Typical Procedure for Direct Geminal Diallylation of Propiophenone. Procedure A (Table 1, run 1): To a solution of $VCl_2(tmeda)_2$ (1.4 g, 4.0 mmol) in THF (40 mL) at 20 °C was added propiophenone (133 mg, 1.0 mmol) and allyl bromide (0.34 mL, 3.9 mmol). The reaction mixture was stirred for 18 h at 20 °C and then the resulting purple suspension was refluxed for 12 h. An aqueous NaOH solution (1 mol/L, 1 mL) was added to the resulting reaction mixture and the mixture was stirred at 20 °C for an additional 1 h. The precipitated white solid was removed by filtration and washed with ethyl acetate (10 mL). The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane as an eluent) to afford a diallyl compound **1a** (35 mg, 18%) as colorless oils and unreacted propiophenone (96 mg, 72%).

Procedure B (Table 1, run 3): To a solution of $VCl_2(tmeda)_2$ (941 mg, 2.7 mmol) in THF (30 mL) were added zinc powder (87 mg, 1.3 mmol), propiophenone (89 mg, 0.66 mmol) and allyl bromide (0.24 mL, 2.8 mmol) successively. The reaction mixture was stirred for 30 min at 20 °C and then the resulting purple suspension was refluxed for 12 h. The reaction mixture was stirred at 20 °C for an additional 1 h after addition of an aqueous NaOH solution (1 mol/L, 1 mL). The precipitated white solid was removed by filtration and washed with ethyl acetate (10 mL). The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane as an eluent) to afford a diallyl compound **1a** (78 mg, 59%) and a coupling product **2a** (35 mg, 33%) as colorless oils.

Procedure C (Table 1, run 5, high dilution): To a solution of $VCl_2(tmeda)_2$ (1.3 g, 3.7 mmol) in THF (40 mL) were added zinc powder (123 mg, 1.9 mmol), propiophenone (126 mg, 0.94 mmol) and allyl bromide (0.32 mL, 3.7 mmol) successively. The reaction mixture was stirred for 30 min at 20 °C and the resulting purple suspension was diluted with THF (400 mL). To this was added allyl bromide (0.15 mL, 1.7 mmol) and then the reaction mixture was refluxed for 12 h. The resulting reaction mixture was stirred at 20 °C for an additional 30 min after addition of an aqueous NaOH solution (1 mol/L, 1 mL). The precipitated white solid was removed by filtration and washed with ethyl acetate. The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane as an eluent) to afford a diallyl compound **1a** (157 mg, 84%) and a coupling product **2a** (23 mg, 15%) as colorless oils.

4-Ethyl-4-phenylhepta-1,6-diene (1a): R_f = 0.50 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.68 (t, J = 7.4 Hz, 3H), 1.71 (q, J = 7.4 Hz, 2H), 2.45 (d, J = 7.2 Hz, 4H), 4.95-5.05 (m, 4H), 5.49-5.65 (m, 2H), 7.11-7.31 (m, 5H). HRMS (EI): *m/z* calcd for $C_{15}H_{19}$ (M^+-H) 199.1457, found 199.1487. IR (neat): 3075, 2970, 2930, 1640, 1600, 1500, 1440, 1420, 1380, 1315, 1080, 1040, 1000, 915, 760, 700, and 660 cm^{-1}. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.60; H, 9.84.

4,5-Diethyl-4,5-diphenylocta-1,7-diene (2a): A mixture of two diastereomers (*dl* : *meso* = 50 : 50). R*f* = 0.24 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.67 [t, *J* = 7.4 Hz, 6H (*dl* or *meso*)], 0.72 [t, *J* = 7.4 Hz, 6H (*meso* or *dl*)], 1.91-2.17 (m, 3H), 2.10-2.31 (m, 1H), 2.55-2.97 (m, 4H), 4.79-4.98 [m, 4H (*dl* or *meso*)], 4.95-5.14 [m, 4H (*meso* or *dl*)], 5.52-5.68 [m, 2H (*dl* or *meso*)], 5.68-5.84 [m, 2H (*meso* or *dl*)], 6.66-7.02 (m, 4H), 6.97-7.11 (m, 6H). MS (EI): *m/z* 318 (M^+). IR (neat): 3070, 2975, 2940, 2890, 1640, 1600, 1500, 1460, 1440, 1420, 1400, 1390, 1080, 1040, 1000, 915, 770, and 705 cm^{-1}. Anal. Calcd for $C_{24}H_{30}$: C, 90.51; H, 9.49. Found: C, 90.73; H, 9.25.

Typical Procedure for Scheme 2: To a solution of zinc alkoxide prepared from propiophenone (138 mg, 1.0 mmol), allyl bromide (0.1 mL, 1.1 mmol) and zinc powder (74 mg, 1.1 mmol) in THF (10 mL) was added a solution of $VCl_2(tmeda)_2$ (734 mg, 2.1 mmol) in THF (20 mL) at 20 °C. The color of the reaction mixture changed from blue to green. The reaction mixture was stirred for 1 h at 20 °C and then to this was added allyl bromide (0.36 mL, 4.2 mmol). The reaction mixture was stirred for an additional 1 h at 20 °C and then refluxed for 15 h. An aqueous NaOH solution (1 mol/L, 1 mL) was added and the mixture was stirred at 20 °C for an additional 1 h. The precipitated white solid was removed by filtration and washed with ethyl acetate (10 mL). The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane as an eluent) to afford a diallyl compound **1a** (108 mg, 52%) and a coupling product **2a** (54 mg, 33%) as colorless oils.

Typical procedure for Scheme 3: To a solution of zinc alkoxide prepared from propiophenone (174 mg, 1.3 mmol), allyl bromide (0.12 mL, 1.4 mmol) and zinc powder (90 mg, 1.4 mmol) in THF (8 mL) was added a solution of $VCl_2(tmeda)_2$ (475 mg, 1.3 mmol) in THF (15 mL) at 20 °C. The color of the reaction mixture changed from blue to green. The reaction mixture was stirred for 1 h at 20 °C and then to this was added allylmagnesium bromide (1.0 mol/L, 1.3 mL, 1.3 mmol) at 0 °C. The reaction mixture was stirred for additional 1h at 0°C and then refluxed for 20h. An aqueous NaOH solution (1 mol/L, 1 mL) was added and the mixture was stirred at 20°C for an additional 1h. The precipitated white solid was removed by filtration and washed with ethyl acetate (10 mL). The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane/AcOEt = 20/1 as an eluent) to afford a trace amount of **2a** and the homoallyl alcohol **3** (160 mg, 70%).

Typical Procedure for Construction of an Asymmetric Quaternary Carbon Compound (Table 2, run 1). To a solution of magnesium alkoxide prepared from propiophenone (90 mg, 0.66 mmol), methylmagnesium bromide (0.91 mol/L, 0.80 mL, 0.73 mmol) in THF (8 mL) was added a solution of $VCl_2(tmeda)_2$ (486 mg, 1.4 mmol) in THF (15 mL) at 20 °C. The color of the reaction mixture changed from blue to green. The reaction mixture was stirred for 1 h at 20 °C and then to this was added allyl bromide (0.23 mL, 2.7 mmol). The reaction mixture was stirred for an additional 1 h at 20 °C and then refluxed for 13 h. An aqueous NaOH solution (1 mol/L, 1 mL) was added and the mixture was stirred at 20°C for an additional 1 h. The precipitated white solid was removed by filtration and washed with ethyl acetate (10 mL). The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column

chromatography on silica gel (hexane as an eluent) to afford a methyl allyl compound **7a** (58 mg, 50%) and a coupling product **8a** (41 mg, 46%) as colorless oils.

Typical Procedure for Construction of an Asymmetric Quaternary Carbon Compound: High Dilution Condition (Table 2, run 2). To a solution of magnesium alkoxide prepared from propiophenone (143 mg, 1.1 mmol), methylmagnesium bromide (0.92 mol/L, 1.2 mL, 1.1 mmol) in THF (8 mL) was added a solution of $VCl_2(tmeda)_2$ (757 mg, 2.1 mmol) in THF (22 mL) at 20 °C. The color of the reaction mixture changed from blue to green. The reaction mixture was stirred for 1h at 20 °C and diluted with THF (500 mL). The reaction mixture was stirred for 1 h at 20 °C after addition of allyl bromide (0.38 mL, 4.4 mmol) and then refluxed for 12 h. An aqueous NaOH solution (1 mol/L, 1 mL) was added and the mixture was stirred at 20 °C for an additional 0.5 h. The precipitated white solid was removed by filtration and washed with ethyl acetate. The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane as an eluent) to afford a methyl allyl compound **1b** (112 mg, 60%) and a coupling product **2b** (56 mg, 39%) as colorless oils.

4-Methyl-4-phenylhex-1-ene (1b): R*f* = 0.41 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.66 (t, *J* = 7.4 Hz, 3H), 1.24 (s, 3H), 1.52-1.60 (m, 1H), 1.72-1.80 (m, 1H), 2.28-2.30 (m, 1H), 2.42-2.44 (m, 1H), 4.89-4.98 (m, 2H), 5.51-5.54 (m, 1H), 7.12-7.28 (m, 5H). HRMS (EI): *m/z* calcd for $C_{13}H_{18}$ (M^+) 174.1409, found 174.1418. IR (neat): 3060, 3025, 2960, 2920, 2880, 1640, 1600, 1500, 1460, 1440, 1380, 1040, 1000, 915, 760, and 700 cm^{-1} .

3,4-Dimethyl-3,4-diphenylhexane (2b): A mixture of two diastereomers (*dl* : *meso* = 50 : 50). R*f* = 0.27 (hexane). Mp 55-57 °C. ^{1}H NMR ($CDCl_3$): δ 0.51 (t, *J* = 9.0 Hz, 6H), 1.26 [s, 6H (*dl* or *meso*)], 1.28 [s, 6H (*meso* or *dl*)], 1.41-1.67 (m, 2H), 1.92-2.10 [m, 2H (*meso* or *dl*)], 2.10-2.32 [m, 2H (*dl* or *meso*)], 6.19-7.09 (m, 4H), 7.05-7.26 (m, 6H). MS (EI): *m/z* 133 (M^+-$C_6H_5CC_2H_5CH_3$). IR (nujol): 3080, 3050, 2970, 2920, 2850, 1600, 1500, 1460, 1440, 1380, 1090, 1030, 800, 770, 730, 700, and 620 cm^{-1}. Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.87; H, 9.57.

3-Ethyl-3-phenylhex-1-ene (1c): R*f* = 0.41 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.67 (t, *J* = 7.4 Hz, 6H), 1.69 (q, *J* = 7.4 Hz, 4H), 2.44 (ddd, *J* = 7.2, 1.2, 1.0 Hz, 2H), 4.94-5.05 (m, 2H), 5.50-5.65 (m, 1H), 7.12-7.33 (m, 5H). HRMS (EI): *m/z* calcd for $C_{14}H_{20}$ (M^+) 188.1565, found 188.1536. IR (neat): 3050, 3020, 2960, 2940, 2880, 1640, 1600, 1500, 1460, 1440, 1415, 1380, 1340, 1300, 1080, 1035, 1000, 960, 915, 875, 850, 780, 760, and 700 cm^{-1}.

3,4-Diethyl-3,4-diphenylhexane (2c): R*f* = 0.27 (hexane). Mp 42-44 °C. ^{1}H NMR ($CDCl_3$): δ 0.66 (t, *J* = 7.2 Hz, 12H), 2.00 (q, *J* = 7.2 Hz, 8H), 6.93-7.01(m, 4H), 7.03-7.14 (m, 6H). MS (EI): *m/z* 147 (M^+-$C_6H_5CC_2H_5C_2H_5$). IR (nujol): 3090, 3050, 2900, 2850, 2720, 1600, 1500, 1460, 1380, 760, 720, and 700 cm^{-1}. Anal. Calcd for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.63; H, 10.10.

3,4-Dimethyl-4-phenylhex-1-ene (1d-A) and 5-Methyl-5-phenylhept-2-ene (1d-B): The diastereomers could not be separated and their ratio was determined by ^{1}H NMR analysis. R*f* = 0.41 (hexane).

^{1}H NMR ($CDCl_3$): δ 0.57 [t, J = 7.6 Hz, 3H **A** (*threo* or *erythro*)], 0.65 [t, J = 7.6 Hz, 3H **A** (*erythro* or *threo*)], 0.66 (t, J = 7.3 Hz, 3H **B**), 0.70 [d, J = 6.0 Hz, 3H **A** (*threo* or *erythro*)], 0.93 [d, J = 6.9 Hz, 3H **A** (*erythro* or *threo*)], 1.19 -1.26 (m, 3H **A** + 3H **B**), 1.52-1.96 (m, 2H **A** + 5H **B**), 2.17-2.45 (m, 1H **A** + 2H **B**), 4.80-4.87 (m, 1H **A**), 4.99-5.07 (m, 1H **A**), 5.17-5.23 (m, 1H **B**), 5.34-5.48 (m, 1H **B**), 5.51-5.80 (m, 1H **A**), 7.13-7.33 (m, 5H **A** + 5H **B**). HRMS (EI): *m/z* calcd for $C_{14}H_{20}$ (M^+) 188.1565, found 188.1580. IR (neat): 3090, 3060, 3020, 2960, 2930, 2880, 1600, 1500, 1445, 1380, 1035, 1005, 970, 915, 760, and 700 cm^{-1}.

1,2-Diphenyl-2-methylbutane (1e): Title compound was obtained as a mixture of **1e**, **2b** and dibenzyl. Rf = 0.25 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.69 (t, J = 7.6 Hz, 3H), 1.22 (s, 3H), 1.57-1.62 (m, 1H), 1.88-2.01 (m, 1H), 2.79 (d, J = 13.2 Hz, 1H), 2.94 (d, J = 12.5 Hz, 1H), 6.74-7.30 (m, 10H). HRMS (GC, EI): *m/z* calcd for $C_{17}H_{20}$ (M^+) 224.1565, found 224.1566. IR (neat, mixture): 3090, 3060, 3025, 2960, 2930, 2880, 2850, 1940, 1800, 1600, 1580, 1500, 1455, 1380, 1340, 1080, 1030, 1000, 910, 810, 770, 750, 700, 620, and 610 cm^{-1}.

4-Methyl-4-phenylhex-1-yne (1f-A): Rf = 0.18 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.68 (t, J = 7.6 Hz, 3H), 1.41 (s, 3H), 1.69-1.89 (m, 2H), 1.91 (t, J = 2.6 Hz, 1H), 2.50 (t, J = 2.6 Hz, 2H), 7.16-7.32 (m, 5H). HRMS (EI); *m/z* calcd for $C_{13}H_{16}$ (M^+) 172.1252, found 172.1261. IR (neat): 3300, 3090, 3060, 3020, 2970, 2940, 2880, 2120, 1600, 1500, 1460, 1445, 1380, 1080, 1035, 760, 700, and 630 cm^{-1}.

4-Methyl-4-phenylhexa-1,2-diene (1f-B): Rf = 0.39 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.77 (t, J = 7.6 Hz, 3H), 1.37 (s, 3H), 1.74-1.84 (m, 2H), 4.80 (d, J = 1.3 Hz, 1H), 4.82 (d, J = 1.3 Hz, 1H), 5.37 (t, J = 6.6 Hz, 1H), 7.18-7.38 (m, 5H). HRMS (EI): *m/z* calcd for $C_{13}H_{16}$ (M^+) 172.1252, found 172.1279. IR (neat): 3090, 3060, 3030, 2970, 2940, 2880, 1960, 1600, 1500, 1450, 1385, 1040, 850, 760, and 700 cm^{-1}.

4,4,4-Triphenylbut-1-ene (1g): Rf = 0.27 (hexane/AcOEt = 10/1). Mp 61-63 °C. ^{1}H NMR ($CDCl_3$): δ 3.47 (dt, J = 6.7, 1.5 Hz, 2H), 4.94-5.08 (m, 2H), 5.58-5.76 (m, 1H), 7.14-7.32 (m, 15H). HRMS (EI): *m/z* calcd for $C_{22}H_{20}$ (M^+) 284.1565, found 284.1537. IR (nujol): 3050, 3030, 2970, 2920, 2880, 1955, 1890, 1810, 1630, 1595, 1495, 1440, 1315, 1190, 1160, 1115, 1080, 1030, 1000, 965, 910, 850, 820, 760, 730, 700, 660, 630, 620, and 610 cm^{-1}. Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.82; H, 7.12.

4,4-Diphenylbut-1-ene (1h): Rf = 0.59 (hexane/AcOEt = 10/1). ^{1}H NMR ($CDCl_3$): δ 2.77-2.84 (m, 2H), 4.00 (t, J = 7.9 Hz, 1H), 4.90-5.05 (m, 2H), 5.63-5.76 (m, 1H), 7.11-7.29 (m, 10H). HRMS (EI): *m/z* calcd for $C_{16}H_{16}$ (M^+) 208.1252, found 208.1246. IR (neat): 3060, 3025, 2980, 2920, 1640, 1600, 1500, 1450, 1080, 1040, 1000, 920, 845, 790, 740, and 700 cm^{-1}.

1,1,2,2-Tetraphenylethane (2h):[20] Rf = 0.23 (hexane/AcOEt = 10/1). Mp 212-213 °C. ^{1}H NMR ($CDCl_3$): δ 4.76 (s, 2H), 7.01-7.17 (m, 20H). IR (neat): 3080, 3020, 2910, 2850, 1600, 1500, 1450, 1380, 1260, 1070, 1030, 800, 740, 700, and 600 cm^{-1}.

Typical Procedure for Equation 3. To a solution of magnesium alkoxide prepared from benzalacetone (162 mg, 1.1 mmol), methylmagnesium bromide (0.91 mol/L, 1.3 mL, 1.2 mmol) in THF (10 mL) was added a solution of $VCl_2(tmeda)_2$ (786 mg, 2.2 mmol) in THF (20 mL) at 20 °C. The color of the reaction mixture changed from blue to green. The reaction mixture was stirred for 1h at 20 °C and to this was added allyl bromide (0.38 mL, 4.4 mmol). The reaction mixture was stirred for 1 h at 20 °C and then refluxed for 4 h. An aqueous NaOH solution (1 mol/L, 1 mL) was added and the mixture was stirred at 20 °C for an additional 1 h. The precipitated white solid was removed by filtration and washed with ethyl acetate. The combined filtrate and washings were concentrated *in vacuo*. The residual oil was purified by column chromatography on silica gel (hexane as an eluent) to afford the mixture of **7** and **8** (76 mg, 37%) as colorless oils. A mixture of the homocoupling products of the α,β-unsaturated ketone also formed concomitantly in 35% yield.

3,3-Dimethyl-1-phenylhexa-1,5-diene (7) and 6-Methyl-4-phenylhepta-1,5-diene (8): The two diastereomers could not be separated and their ratio was determined by ^1H NMR analysis; **7** : **8** = 33 : 67. R_f = 0.51 (hexane/AcOEt = 20/1). ^1H NMR ($CDCl_3$): δ 1.19 (s, 6H **7**), 1.73 (d, J = 1.2 Hz, 3H **8**), 1.80 (d, J = 1.2 Hz, 3H **8**), 2.23 (dt, J = 7.4, 1.0 Hz, 2H **7**), 2.45-2.54 (m, 2H **8**), 3.62-3.65 (m, 1H **8**), 5.00-5.15 (m, 2H **7** + 2H **8**), 5.37-5.42 (m, 1H **8**), 5.75-5.85 (m, 1H **7** + 1H **8**), 6.32 (d, J = 16.1 Hz, 1H **7**), 6.36 (d, J = 16.1 Hz, 1H **7**), 7.21-7.46 (m, 5H **7** + 5H **8**). HRMS (EI): *m/z* calcd for $C_{14}H_{18}$ (M^+) 186.1409, found 186.1396. IR (neat): 3060, 3020, 2950, 2900, 1640, 1600, 1490, 1440, 1380, 990, 965, 910, 745, and 690 cm^{-1}.

3-Methyl-1-phenylhexa-1,5-diene (13) and 4-Phenylhepta-1,5-diene (14): The two diastereomers could not be separated and their ratio was determined by ^1H NMR analysis; **13** : **14** = 52 : 48. R_f = 0.43 (hexane). ^1H NMR ($CDCl_3$): δ 1.09 (d, J = 6.6 Hz, 3H **13**), 1.63-1.67 (m, 3H **14**), 2.08-2.25 (m, 2H **13**), 2.34-2.50 (m, 1H **13** + 2H **14**), 3.28 [dd, J = 7.6, 7.3 Hz, 1H **14** (*cis* or *trans*)], 3.63-3.72 [m, 1H **14** (*trans* or *cis*)], 4,91-5.07 (m, 2H **13** + 2H **14**), 5.39-5.88 (m, 1H **13** + 3H **14**), 6.09-6.18 (m, 1H **13**), 6.35 (d, J = 16.2 Hz, 1H **13**), 7.12-7.37 (m, 5H **13** + 5H **14**). HRMS (EI): *m/z* calcd for $C_{13}H_{16}$ (M^+) 172.1252, found 172.1283. IR (neat): 3077, 3026, 2964, 2923, 1694, 1639, 1601, 1493, 1450, 1416, 1375, 1318, 1288, 1071, 1029, 994, 996, 912, 747, 714, and 694 cm^{-1}.

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