Highly Stereocontrolled Synthesis of (2*E*,4*Z*)-Dienoic Esters with Alumina Catalyst. Its Application to Total Syntheses of Flavor Components and Insect Pheromones[1]

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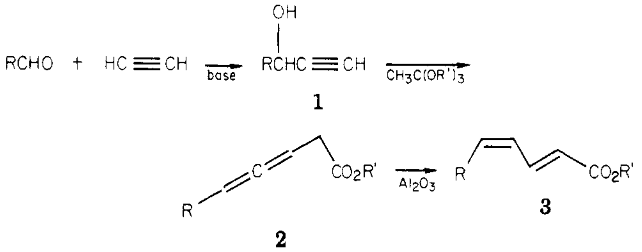
Thermal treatment of β-allenic esters **2** with alumina catalyst in aprotic solvent yielded (2*E*,4*Z*)-dienoic esters **3** in 57–87% yields with 91–100% stereoselectivity. This experimentally simple and economically feasible (2*E*,4*Z*)-dienoate synthesis is illustrated with eight examples. The mechanism of this stereocontrolled rearrangement of **2** to **3** is shown in Scheme I. This synthetic approach to (2*E*,4*Z*)-dienoates was adapted to the simple syntheses of several natural products such as ethyl (2*E*,4*Z*)-decadienoate (**3e**), (2*E*,4*Z*)-decadienal (**8**), (2*E*,4*Z*)-heptadienal (**7**), (7*E*,9*Z*)-dodecadienyl acetate (**9**), and bombykol (**10**) (Scheme II).

(2*E*,4*Z*)-Dienoic esters are important compounds having utility as aroma agents for food, drinks, and tobacco.[2] Certain insect pheromones such as bombykol and (7*E*,9*Z*)-dodecadien-1-yl acetate also have conjugated *E*,*Z*-diene systems.[3-5] Recently, several novel syntheses of (*E*,*Z*)-diene compounds have been reported.[6,7] However, most of the conventional procedures involve Wittig reactions[2f,3-5,8] and/or the reduction of acetylenes[3,5,9-11] as the steps to introduce conjugated diene systems. The former procedures usually give a mixture of geometrical isomers,[3a] while the latter are not suitable for large-scale preparations.

In this paper we report an experimentally simple and economically feasible synthesis of (2*E*,4*Z*)-dienoic esters **3** and the application of this approach to syntheses of several natural products such as aroma agents of food and insect pheromones. The method merely involved the thermal treatment of β-allenic esters **2** with the alumina catalyst[12] (4–7 equiv) in an aprotic solvent, which induces a prototropic rearrangement to give (2*E*,4*Z*)-dienoic esters **3** in good yields. The allenic esters **2** can be readily obtained from trialkyl orthoacetates and propargyl alcohols (**1**)[13] by the Claisen rearrangement.[14-17]



We investigated eight examples of the prototropic rearrangement of **2** to **3** with alumina catalyst. The results of the reaction are summarized in Table I. Although the rearrangments of β-allenic esters to 2,4-dienoates under acidic or basic conditions are well-known,[16,17,19] the stereoselectivities hitherto reported are not satisfactory. For example, Amos and Katzenellenbogen[19] reported that the treatment of ethyl 3,4-decadienoate with sodium ethoxide gave a mixture of 2*Z*,4*E*, 2*E*,4*Z*, and 2*E*,4*E* isomers (6:63:31). Therefore, our results obtained with alumina catalyst are superior to others[16,17,19] because of the high stereoselectivity (91–100%) observed.

The stereochemistry of **3** was determined by ^{1}H NMR spectral data, which showed characteristic signals of quartets at ca. 7.5 ppm due to the C_β H, indicating α,β-trans geometry (J = 16.0 Hz). Furthermore, the ^{1}H NMR spectrum of **3c** was carefully examined by using a shift reagent, europium dipivaloylmethanate (Eu(dpm)) and the proton decoupling technique. The finely resolved spectrum of **3c** containing 0.2 equiv of Eu(dpm) disclosed that the geometry of the γ,δ double bond is cis (J = 11.5 Hz).

To the best of our knowledge, only one example of the alumina-catalyzed synthesis of conjugated dienes from allenes has been reported. Thus Zakharova et al.[20] have described the predominant formation of α,β-cis-conjugated ketones from β-allenic ketones. Their results are quite in

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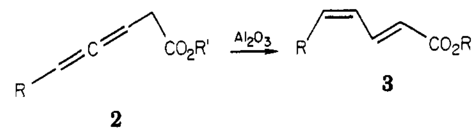
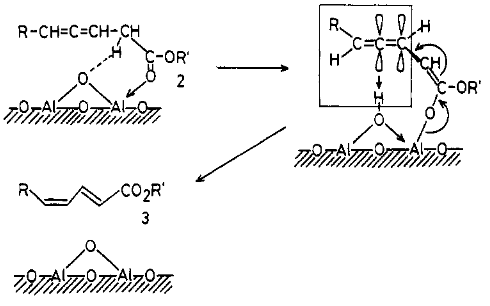
Table I. Rearrangement of Allenic Esters 2 to (2*E*,4*Z*)-Dienoic Esters 3 with Alumina Catalyst



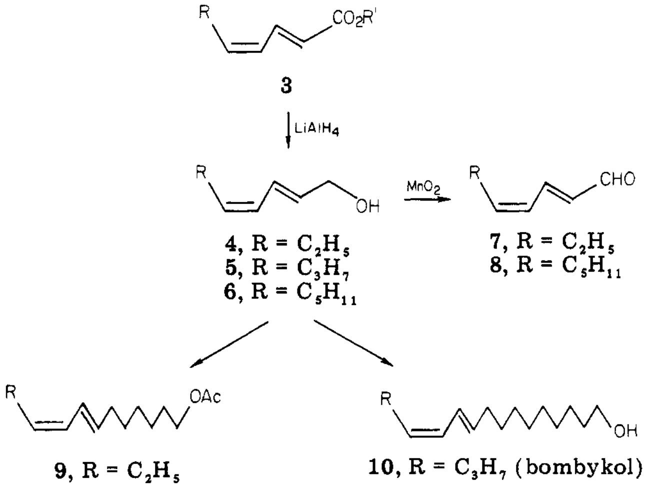
compd[a]	R	R'	reaction conditions[b]: Al_2O_3/2[c]	reaction conditions[b]: time, h	yield,[d] %	purity,[e] %	IR (neat), cm^{-1}	^1H NMR ($CDCl_3$),[l] ppm
3a[f,g]	CH_3	CH_3	4.1	4	57[h]	100	1720, 1640, 1610	1.86 (d, 3, *J* = 5.5), 3.68 (s, 3), 5.50-6.45 (m, 2), 5.77 (d, 1, *J* = 15.5), 7.55 (dd, 1, *J* = 10.5, 15.5)
3b[f]	C_2H_5	CH_3	5.0	4	82	96	1730, 1641, 1610	1.04 (t, 3, *J* = 7), 2.32 (m, 2), 3.74 (s, 3), 5.55-6.35 (m, 2), 5.85 (d, 1, *J* = 15.3), 7.64 (dd, 1, *J* = 10, 15.3)
3c[i]	C_3H_7	CH_3	4.5	2	80	96	1720, 1635, 1605	0.93 (t, 3, *J* = 6), 1.40 (m, 2), 2.22 (m, 2), 3.65 (s, 3), 5.74 (m, 1), 5.75 (d, 1, *J* = 16), 6.12 (t, *J* = 11.5), 7.50 (dd, 1, *J* = 11.5, 16)
3d[i]	C_3H_7	C_2H_5	5.0	4	69	93	1720, 1640, 1610	1.06 (t, 3, *J* = 6), 1.29 (t, 3, *J* = 7), 1.42 (m, 2), 2.26 (m, 2), 4.15 (q, 2, *J* = 7), 5.50-6.40 (m, 2), 5.77 (d, 1, *J* = 16), 7.50 (dd, 1, *J* = 10.5, 16)
3e[j,k]	C_5H_{11}	C_2H_5	6.2	5	82	100	1710, 1634, 1600	0.92 (t, 3, *J* = 5), 1.28 (t, 3, *J* = 7), 1.0-1.7 (m, 6), 2.30 (m, 2), 4.13 (q, 2, *J* = 7), 5.50-6.40 (m, 2), 5.76 (d, 1, *J* = 15), 7.49 (dd, 1, *J* = 10, 15)
3f[f]	C_6H_{13}	CH_3	5.8	2	82	99	1720, 1635, 1605	0.92 (t, 3, *J* = 5), 1.32 (m, 8), 2.30 (m, 2), 3.65 (s, 3), 5.50-6.30 (m, 2), 5.73 (d, 1, *J* = 16), 7.47 (dd, 1, *J* = 11.5, 16)
3g[i]	C_8H_{17}	CH_3	7.2	5	87	91	1720, 1635, 1605	0.92 (t, 3, *J* = 5), 1.32 (br s, 12), 2.30 (m, 2), 3.65 (s, 3), 5.55-6.35 (m, 2), 5.82 (d, 1, *J* = 16), 7.47 (dd, 1, *J* = 11.5, 16)
3h[i]	C_9H_{19}	CH_3	4.7	5	70	96	1720, 1620, 1603	0.90 (t, 3, *J* = 5.5), 1.30 (br s, 14), 2.30 (m, 2), 3.70 (s, 3), 5.50-6.30 (m, 2), 5.78 (d, 1, *J* = 16), 7.53 (dd, 1, *J* = 10.5, 16)

[a] All of compounds **3** are known compounds, but no spectral data are given in the literature unless otherwise indicated. [b] Heated at reflux temperature of benzene. [c] Mole ratio of Al_2O_3/**2**. [d] Isolated yield. [e] Percentage of the 2*E*,4*Z* isomer, determined by GLC analysis. The minor component (lower t_R) was identified as the 2*E*,4*E* isomer. [f] See ref 2d. [g] Spectral data were identical with those of the literature: Naf, F.; Degen, P. *Helv. Chim. Acta* **1971**, *54*, 1939. [h] Lower yield probably due to higher volatility of the product. [i] See ref 2e. [j] See ref 2f, 18, and 19. [k] Spectral data were identical with those of the literature.[18] [l] Multiplicities, the number of hydrogens, and coupling constants (in hertz) are given in parentheses.

Scheme I



Scheme II. Total Syntheses of Several Natural Products



contrast with ours,[21] but the explanation for this stereochemical dissimilarity is not readily apparent. The mechanism we currently prefer for the present highly stereoselective transformation is shown in Scheme I. In analogy with and by combination of the mechanisms proposed by Katzenellenbogen[19] for the rearrangement of allenic esters and by Posner[22] for the role of the alumina catalyst, it is suggested that the first step may be the coordination of the carbonyl oxygen of **2** to the alumina surface followed by a proton shift to produce an enolate intermediate. The subsequent approach of the proton to the central carbon of the allene would be expected to occur

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[21] We carried out the rearrangement of **2** to **3** under the reaction conditions of the literature.[20] Treatment of **2g** with Al_2O_3 (absolute EtOH, 80 °C) resulted in the recovery of **2g** after 4 h and in the formation of **3g** in a poor yield (24%) after 15 h (30% recovery of **2g**).

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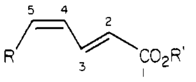
Table IV. ^{13}C NMR Spectral Data of (2*E*,4*Z*)-Dienoates **3**



compd	chemical shift, ppm													
						for R								
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
3a	167.7	120.5	135.8	127.3	139.4	14.0								
3b	167.6	120.7	139.5	125.8	143.1	21.6	13.9							
3c	167.6	121.0	139.7	126.9	141.3	30.3	22.7	13.7						
3e[d]	167.2	121.4	139.5	126.6	141.4	28.3	29.2	31.5	22.6	14.0				
3f	167.7	120.9	139.7	126.6	141.7	28.4	29.5[a]	29.0[a]	31.8	22.7	14.1			
3g	167.8	120.8	139.6	126.5	141.5	28.3	29.4[b]	29.4[b]	29.4[b]	29.2[b]	31.9	22.7	14.0	
3h	167.6	120.8	139.7	126.6	141.7	28.3	29.4[c]	29.6[c]	29.6[c]	29.5[c]	29.5[c]	32.0	22.8	14.0

[a-c] Assignments may be interchangeable. [d] Identical with those of a sample prepared independently (see ref 29).

from the less hindered side (cis),[19] thus leading to the *Z* geometry at the γ,δ bond. The final step to eliminate the enolate of the product from the alumina surface, as visualized by the curved arrows, would produce the thermodynamically more stable *E* geometry at the α,β bond.

This method for preparing (2*E*,4*Z*)-dienoates was adapted to the total syntheses of several natural products, which are outlined in Scheme II. Ethyl (2*E*,4*Z*)-decadienoate (**3e**), a component of the odoriferous principle of Bartlett pears,[23] was stereospecifically prepared in 82% yield, as shown in Table I. Methyl (2*E*,4*Z*)-heptadienoate (**3b**) was converted to (2*E*,4*Z*)-heptadienal (**7**), a flavor component of tomatos.[2a,b,24] Reduction of **3b** with $LiAlH_4$ gave (2*E*,4*Z*)-heptadienol (**4**, 84%), which was subsequently oxidized with active MnO_2 to afford **7** (81%) along with 6% of the 2*E*,4*E* isomer. The acetate of **4** can be converted to (7*E*,9*Z*)-dodecadienyl acetate (**9**), which is the sex pheromone of *Lobesia botrana*, a major pest of vineyards.[25] Furthermore **3e** was converted to (2*E*,4*Z*)-decadienal (**8**), a flavor component of groundnuts and carrot root.[2c] Reduction of **3e** with $LiAlH_4$ gave (2*E*,4*Z*)-decadienol (**6**)[26] in 84% yield, and the subsequent oxidation of **6** with active MnO_2 afforded **8** in 71% yield containing the 2*E*,4*E* isomer (12%). The current reaction was further applied to the preparation of a key intermediate for the synthesis of (10*E*,12*Z*)-hexadecadien-1-ol, which is the sex pheromone of *Bombyx mori*,[5,27] which is called bombykol (**10**). Reduction of methyl (2*E*,4*Z*)-octadienoate (**3c**) with $LiAlH_4$ gave (2*E*,4*Z*)-octadienol (**5**, 89%)[9] which can be converted to bombykol (**10**) in two steps by the known method.[9]

As a part of a continuing ^{13}C NMR study of organic compounds, the ^{13}C NMR spectra of compounds prepared in this work were measured and tentatively assigned as shown in Tables II–IV (Tables II and III are available as supplementary material). Although the differentiation between the chemical shifts of saturated carbons has remained difficult, the signals of unsaturated carbons were completely assigned. Signals of the two acetylene carbons of compounds **1** with the exception of **1a** appeared in the expected ranges,[28] 72.65 ± 0.05 and 85.25 ± 0.15 ppm. Signals of the C_2–C_5 carbons of β-allenic esters **2c**–**h** shifted downfield as the number of alkyl carbons increases, as shown in Table III. Allene carbons C_3 and C_5 were tentatively assigned with consideration of the inductive effect of the ester group. Chemical shifts of olefin carbons in (2*E*,4*Z*)-dienoates **3** were determined with the aid of highly selective proton decoupling, as shown in Table IV. Signals for C_2–C_5 of **3c**–**h** appeared at 121.1 ± 0.3, 139.6 ± 0.1, 126.7 ± 0.2, and 141.5 ± 0.2 ppm, respectively. Chemical shifts, except that of C_2, are 1.8–5.6 ppm upfield from the ordinary positions in the corresponding (2*E*,4*E*)-dienoates.[29] Especially, the signals of C_3 and C_6 undergo large upfield (4.7–5.6 ppm) shifts which result from the steric effect of the cis form.[29,30] These facts afford additional support for assigning the 2*E*,4*Z* geometry of **3**.

Experimental Section

The melting points and boiling points are uncorrected. Elemental analyses were carried out by Mr. Eiichiro Amano of our laboratory. Analytical determinations by GLC were performed on a Hitachi Model K-53 gas chromatograph fitted with a 10% Apiezon L grease on Chromosorb W column (3 mm o.d. × 1 m) or a 10% SE-30 on Chromosorb W column (3 mm o.d. × 1 m). ^1H NMR spectra (60 MHz) were recorded with a Hitachi Model R-24 apparatus. ^{13}C NMR spectra were obtained with a JEOL LTD. JNM-FX100 apparatus, with $CDCl_3$ as a solvent. All chemical shifts are reported in δ units downfield from internal Me_4Si, and the *J* values are given in hertz. Propargyl alcohols **1** were prepared by the method in the literature.[13] Compounds, boiling points, and yields are as follows: **1b**, bp 115–117 °C (lit.[31] bp 121.6–122.0 °C), 37%; **1c**, bp 52–53 °C (20 mm) [lit.[31] bp 50 °C (30 mm)], 72%; **1e**, bp 75–85 °C (15 mm) [lit.[19] bp 60 °C (12 mm)], 54%; **1f**,[32] bp 86–90 °C (12 mm), 25%; **1g**,[32] bp 83–88 °C (5 mm), 37%.

1-Dodecyn-3-ol (1h). To a solution of ethynylmagnesium bromide in 30 mL of THF, prepared from 0.055 mol of ethyl bromide, magnesium, and acetylene,[33] was added in 30 min 6.24 g (0.040 mol) of freshly distilled *n*-decanal under an atmosphere of acetylene. The temperature of the reaction mixture was maintained between 0 and 5 °C during this addition. The solution was allowed to warm to room temperature, and stirring was continued overnight. The reaction mixture was then poured into a solution of 3 g of NH_4Cl in 10 mL of water, and the organic layer

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was extracted with ether. The combined ethereal layers were washed with water and dried over $MgSO_4$. After removal of the solvent, the residual oil was distilled, giving 6.20 g (85%) of **1h** as a clean oil: bp 100–101 °C (1 mm); IR (neat) 3300 (OH), 2080 cm^{-1} ($C{\equiv}C$); ^1H NMR (CCl_4) δ 0.90 (t, J = 5.5 Hz, CH_3), 1.30 (m, $-(CH_2)_8-$), 1.59 (s, OH), 2.28 (d, J = 2 Hz, $C{\equiv}CH$), 4.25 (m, CHOH). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.00; H, 12.21.

β-Allenic ester (2) was prepared by the method described in literature.[14,15] A mixture of **1**, 6–7 equiv of trimethyl orthoacetate or triethyl orthoacetate, and a catalytic amount of propionic acid (ca. 0.003 equiv) was heated to ca. 130–150 °C for 7–30 h with removal of alcohol by distillation. The allenic esters were separated by distillation. Compounds, boiling points, yields, and spectral data are as follows. **2a**:[34] bp 61–62 °C (11 mm); 69%; IR (neat) 1978 ($C{=}C{=}C$), 1742 (CO_2CH_3), 1170 cm^{-1}; ^1H NMR (CCl_4) δ 1.65 (m, 3 H, CH_3), 2.95 (m, 2 H, $C\mathbf{H}_2CO_2CH_3$), 3.66 (s, 3 H, CO_2CH_3), 5.14 (m, 2 H, $CH{=}C{=}CH$). **2b**:[35] bp 100–103 °C (50 mm); 67%; IR (neat) 1970 ($C{=}C{=}C$), 1742 cm^{-1} (ester $C{=}O$); ^1H NMR (CCl_4) δ 1.0 (t, J = 7 Hz, 3 H, CH_3), 2.01 (m, $C\mathbf{H}_2CH{=}$), 2.90 (dd, J = 4, 5.5 Hz, 2 H, $C\mathbf{H}_2CO_2CH_3$), 3.60 (s, 3 H, OCH_3), 5.15 (m, $CH{=}C{=}CH$). **2c**:[34] bp 130 °C (25 mm); 52%; IR (neat) 1970 ($C{=}C{=}C$), 1740 cm^{-1} ($C{=}O$); ^1H NMR (CCl_4) δ 0.92 (t, 3 H, CH_3), 1.42 (m, 2 H, $CH_3C\mathbf{H}_2$), 1.95 (m, 2 H, $C\mathbf{H}_2CH{=}$), 2.90 (m, 2 H, $C\mathbf{H}_2CO_2CH_3$), 3.59 (s, 3 H, OCH_3), 5.08 (m, 2 H, $CH{=}C{=}CH$). **2d**:[34] bp 140 °C (bath temperature; 15 mm); 76%; IR (neat) 1970 ($C{=}C{=}C$), 1740 cm^{-1} (ester $C{=}O$); ^1H NMR (CCl_4) δ 0.94 (t, J = 5 Hz, 3 H, CH_3), 1.27 (t, J = 7 Hz, 3 H, $CO_2CH_2C\mathbf{H}_3$), 1.30 (m, 2 H, $CH_3C\mathbf{H}_2CH_2$), 1.96 (m, 2 H, $C\mathbf{H}_2CH{=}$), 2.91 (dd, J = 4, 5.5 Hz, 2 H, ${=}CHC\mathbf{H}_2CO_2Et$), 4.11 (q, 2 H, $CO_2C\mathbf{H}_2CH_3$), 5.13 (m, 2 H, $CH{=}C{=}CH$). **2e**: bp 84 °C (5 mm); 88%; IR and ^1H NMR data were identical with those of the literature.[15] **2f**:[15] bp 140 °C (bath temperature; 5 mm); 53%; spectral data were identical with those of the literature.[15] **2g**:[36] bp 140 °C (bath temperature; 5 mm); 86%; IR (neat) 1970 ($C{=}C{=}C$), 1740 cm^{-1} ($C{=}O$); ^1H NMR (CCl_4) δ 0.92 (t, J = 5 Hz, 3 H, $(CH_2)_7C\mathbf{H}_3$), 1.30 (br s, 12 H, $(C\mathbf{H}_2)_6CH_3$), 1.97 (m, 2 H, $C\mathbf{H}_2(CH_2)_6CH_3$), 2.91 (m, 2 H, $C\mathbf{H}_2CO_2CH_3$), 3.62 (s, 3 H, CO_2CH_3), 5.11 (m, 2 H, $CH{=}C{=}CH$). See the paragraph at the end of the paper about supplementary material.

Methyl 3,4-Tetradecadienoate (2h). A mixture of 0.72 g (4.0 mmol) of **1h**, trimethyl orthoacetate (3.0 g, 25 mmol), and a catalytic amount of propionic acid was heated at reflux temperature for 30 h, removing methanol twice by distillation. After removal of the excess of trimethyl orthoacetate, the residue was distilled to give 0.82 g (86%) of **2h**: bp 130 °C (bath temperature; 0.1 mm); IR (neat) 1975 ($C{=}C{=}C$), 1745 (ester $C{=}O$), 1166 cm^{-1}; ^1H NMR (CCl_4) δ 0.89 (br t, 3 H, $CH_2C\mathbf{H}_3$), 1.25 (br s, 14 H, $(C\mathbf{H}_2)_7CH_3$), 1.95 (m, 2 H, $C\mathbf{H}_2(CH_2)_7CH_3$), 2.90 (m, 2 H, $C\mathbf{H}_2CO_2CH_3$), 3,61 (s, 3 H, CO_2CH_3), 5.11 (m, 2 H, $CH{=}C{=}CH$). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.78; H, 10.82.

General Procedure for the Transformation of 2 to 3. The allenic esters **2** were heated with alumina[12] (4–7 equiv) at the reflux temperature of benzene. The reaction was monitored by IR or NMR spectrum and terminated as soon as the starting material disappeared. Usually it took 2–5 h. After cooling, the alumina catalyst was removed by filtration, and the evaporation of the solvent gave the ^1H NMR pure **3** as a clean oil. The following experiment is typical one.

Ethyl (2*E*,4*Z*)-Octadienoate (3d). A mixed solution of 0.18 g (1.17 mmol) of **2d**, 0.6 g of alumina, and 5 mL of dry benzene was heated at reflux temperature for 4 h. The mixture was filtered, and the filtrate was concentrated in vacuo to give 0.125 g (69%) of **3d**[2f,37] as a clean oil. Spectral data are tabulated in Table I.

(2*E*,4*Z*)-Heptadienol (4). To a stirred mixture of 89 mg (2.34 mmol) of $LiAlH_4$ and 1 mL of dry ether was added dropwise a solution of 0.3 g (2.14 mmol) of **3b** in 1 mL of dry ether at −40 °C. The mixture was stirred for 1.5 h at −40 °C and then quenched with 10% HCl. The organic layer was extracted with ether, and the combined ethereal layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave 0.202 g (84%)[38] of **4**:[11] IR (neat) 3330 (OH), 1638 cm^{-1} ($C{=}C$); ^1H NMR (CCl_4) δ 1.0 (t, J = 7 Hz, 3 H, CH_3), 2.20 (m, 2 H, CH_2CH_3), 3.76 (s, 1 H, OH), 4.07 (d, 2 H, J = 5 Hz, CH_2OH), 5.0–6.8 (m, 4 H, olefin protons); ^{13}C NMR[38] ($CDCl_3$) δ 14.2 (q, CH_3), 21.1 (t, $\mathbf{CH_2}CH_3$), 63.2 (t, CH_2OH), 126.5 (d, ${=}CH$), 127.2 (d, ${=}CH$), 131.8 (d, ${=}CH$), 134.3 (d, ${=}CH$).

(2*E*,4*Z*)-Heptadienal (7). A mixture of 0.7 g of activated manganese dioxide and 10 mL of petroleum ether was added to 70 mg (0.625 mmol) of **4**. The mixture was stirred for 1 h at room temperature and then filtered. The filtrate was concentrated in vacuo to give 60 mg (87%) of **7** containing ca. 6% of the *E*,*E* isomer. IR spectrum was identical with that of the authentic sample:[2a] ^1H NMR (CCl_4) δ 1.09 (t, 3 H, J = 7 Hz, $CH_2C\mathbf{H}_3$), 2.30 (m, 2 H, $C\mathbf{H}_2CH_3$), 5.5–6.4 (m, C_α H, C_γ H, C_δ H), 7.32 (dd, 1 H, J = 10.5, 15.6 Hz, C_β H), 9.49 (d, 1 H, J = 8 Hz, CHO).

(2*E*,4*Z*)-Decadienol (6). A mixture of 0.502 g (2.75 mmol) of **3e** and 0.104 g (2.75 mmol) of $LiAlH_4$ was stirred for 1 h at −30 °C. The mixture was quenched with 10% HCl, and the organic layer was extracted with ether. The combined ethereal layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave **6**:[26] 0.356 g (84%); clean oil; IR (neat) 3300 cm^{-1} (OH); ^1H NMR (CCl_4) δ 0.90 (t, J = 6 Hz, 3 H, CH_3), 1.35 (m, 6 H, $(C\mathbf{H}_2)_3CH_3$), 2.15 (m, 2 H, $C\mathbf{H}_2(CH_2)_3CH_3$), 3.23 (s, 1 H, OH), 4.09 (d, J = 5.5 Hz, 2 H, CH_2OH), 5.05–6.80 (m, 4 H, olefin protons).

(2*E*,4*Z*)-Decadienal (8).[2c] A mixture of 40 mg (0.26 mmol) of **6**, 0.4 g (4.4 mmol) of active manganese dioxide, and 3 mL of petroleum ether was stirred for 1.5 h at room temperature. The mixture was filtered, and concentration of the filtrate gave 28 mg (71%) of **8**:[26,39] IR (neat) 1675 ($CH{=}O$), 1628 cm^{-1} ($C{=}C$); NMR (CCl_4) δ 0.91 (t, J = 5 Hz, 3 H, CH_3), 1.35 (m, 6 H, $(CH_2)_3$), 2.32 (m, 2 H, $C\mathbf{H}_2CH{=}$), 6.1 (m, 3 H, olefin protons), 7.41 (dd, J = 10, 15 Hz, 1 H, C_β H), 9.56 (d, J = 8 Hz, CHO).

(2*E*,4*Z*)-Octadienol (5). To a stirred mixture of 0.17 g (4.48 mmol) of $LiAlH_4$ and 10 mL of dry ether was added a solution of 0.69 g (4.48 mmol) of **3c** in 3 mL of dry ether at −30 to −40 °C. After 1.5 h, the reaction mixture was quenched with 1 mL of ethyl acetate and neutralized with dilute HCl. The organic layer was extracted with ether, and the combined ethereal layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave 0.50 g (89%) of **5**: ^{13}C NMR ($CDCl_3$) δ 13.7 (q, CH_3), 22.9 (t, $CH_3\mathbf{CH_2}CH_2$), 29.9 (t, $\mathbf{CH_2}CH_2CH_3$), 63.6 (t, CH_2OH), 127.0 (d, $\mathbf{CH}{=}CHCH_2OH$), 127.9 (d, ${=}\mathbf{C}HCH{=}CHCH_2OH$), 131.7 (d, $CH{=}\mathbf{C}HCH_2OH$), 132.9 (d, $\mathbf{CH}{=}CHCH{=}CHCH_2OH$). The ^1H NMR spectrum was identical with that of an authentic sample.[9a]

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Registry No. 1a, 2028-63-9; **1b**, 4187-86-4; **1c**, 105-31-7; **1e**, 818-72-4; **1f**, 7383-20-2; **1g**, 53735-49-2; **1h**, 81929-17-1; **2a**, 81981-05-7; **2b**, 81981-06-8; **2c**, 81981-07-9; **2d**, 30333-00-7; **2e**, 36186-28-4; **2f**, 81981-08-0; **2g**, 81981-09-1; **2h**, 81981-10-4; (*E*,*Z*)-**3a**, 30361-31-0; (*E*,*Z*)-**3b**, 39924-42-0; (*E*,*E*)-**3b**, 56424-97-6; (*E*,*Z*)-**3c**, 39924-43-1; (*E*,*E*)-**3c**, 74418-28-3; (*E*,*Z*)-**3d**, 39924-38-4; (*E*,*E*)-**3d**, 60388-61-6; (*E*,*Z*)-**3e**, 3025-30-7; (*E*,*Z*)-**3f**, 39924-46-4; (*E*,*E*)-**3f**, 77811-09-7; (*E*,-

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(34) This compound is mentioned in ref 14, but no physical data are given.

(35) This compound is mentioned in ref 17, but no spectral data are given.

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(37) GLC analysis (column, 10% SE-30 on Chromosorb W, 100 °C; carrier gas, N_2 20 mL/min) showed two peaks at t_R 6.8 (93%) and 9.3 min (7%). The minor component was isolated by preparative GLC and identified as the 2*E*,4*E* isomer by comparison of the ^1H NMR spectrum and the t_R with those of a sample prepared independently.[29]

(38) The ^{13}C NMR spectrum suggested the existence of the 2*E*,4*E* isomer (6%) as a minor product.

(39) GLC analysis (column, 150 °C; carrier gas, He, 25 mL/min) showed two peaks at t_R 12.8 (88%) and 16.0 min (12%). The minor component is thought to be 2*E*,4*E* isomer.

Z)-**3g**, 55025-21-3; (*E*,*E*)-**3g**, 81981-11-5; (*E*,*Z*)-**3h**, 54977-81-0; (*E*,*E*)-**3h**, 24738-47-4; (*E*,*Z*)-**4**, 70979-88-3; (*E*,*E*)-**4**, 33467-79-7; (*E*,*Z*)-**5**, 56904-85-9; (*E*,*Z*)-**6**, 16195-71-4; (*E*,*Z*)-**7**, 4313-02-4; (*E*,*E*)-**7**, 4313-03-5; (*E*,*Z*)-**8**, 25152-83-4; (*E*,*E*)-**8**, 25152-84-5; ethynyl bromide, 593-61-3; decanal, 112-31-2; trimethyl orthoacetate, 1445-45-0; triethyl orthoacetate, 78-39-7.

Supplementary Material Available: Tables II and III containing ^{13}C NMR data for compounds **1** and **2** (2 pages). Ordering information is given on any current masthead page.

Selectivity in the Allylic Substitutions with Organometallics through Neighboring Coordination. 2-(Allyloxy)benzothiazoles as S_N2' Electrophiles for Regio- and Stereoselective Olefin Syntheses

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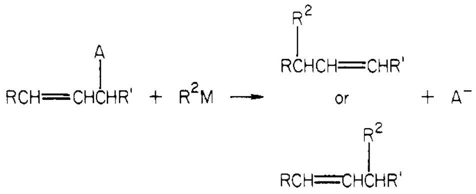
An efficient control of the regio- and stereochemistry in the allylic substitutions with organomagnesium compounds has been achieved by using 2-(allyloxy)benzothiazoles as substrates in the presence of copper bromide. The selectivity is due to the coordinative effects of the substrates toward the organometallic species.

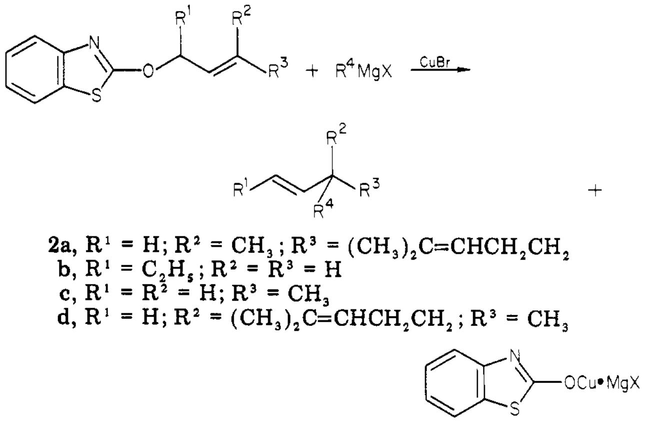
Reacton of organomagnesium compounds with allylic ethers in the presence of a catalytic amount of copper(I) salts has been utilized as facile method for the formation of a new carbon–carbon bond.[2] But the competitive α/γ substitution by the Grignard reagent at the allylic system[3-5] has precluded a wider acceptance of the method. In fact, an extensive study[6] of a wide variety of allylic ethers revealed that the α/γ ratio was a sensitive function of stereic effects in the ether. Another severe limitation[4,6] is represented, except in a special case,[7] by the lack of stereoselectivity accompanying the S_N2' process in noncyclic allylic ethers. These drawbacks could potentially be surmounted by using an allylic substrate bearing a substituent with coordinating properties for the organometallic which could improve the positional selectivity.[8] It should also be preferable for synthetic purposes that this substituent could be lost during the C-C coupling process, as depicted in Scheme I.

Scheme I[a]



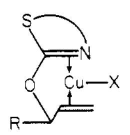
[a] A = a group with coordinating properties toward R^2M.

Scheme II



2a, $R^1 = H; R^2 = CH_3; R^3 = (CH_3)_2C{=}CHCH_2CH_2$
b, $R^1 = C_2H_5; R^2 = R^3 = H$
c, $R^1 = R^2 = H; R^3 = CH_3$
d, $R^1 = H; R^2 = (CH_3)_2C{=}CHCH_2CH_2; R^3 = CH_3$

Recently we have found that some allylic ethers of benzothiazole react with carbon nucleophiles such as cuprates[9] and copper(I) acetylides[10] to give highly selective carbon–carbon coupling reactions. The surprisingly high selectivity found was tentatively explained by us as due to coordination phenomena toward the organometallic species exerted by the benzothiazole allylic ethers. In this regard, we have demonstrated that some 2-(allyloxy)benzothiazoles behave as efficient bidentate ligands for copper(I) halogenides to give stable complexes in which the metal is probably inserted between the C═N of the heterocycle and C═C double bond of the allylic framework.[11] In this paper we describe the reactions of these 2-(allyloxy)benzothiazoles with Grignard reagents in the presence of CuBr and the consequences of the coordination phenomena toward the organometallic species on the re-



R = alkyl; X = Cl, Br, I

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[1] Taken in part from the M.S. Thesis of A.C., University of Bari.

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