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Notes

Alkylation and Silylation of the Aluminum Enolates Generated by Hydroalumination of α,β-Unsaturated Carbonyl Compounds

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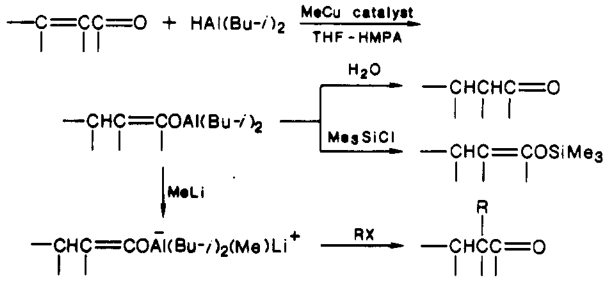
Aluminum enolates are versatile intermediates in organic synthesis and several methods for their generation have been reported. Formation of the less substituted "kinetic" aluminum enolates by means of deprotonation of unsymmetrical ketones by diisobutylaluminum phenoxide–pyridine[1] and diethylaluminum 2,2,6,6-tetramethylpiperidide[2] has been reported. Conjugate addition of aluminum compounds to α,β-enones is another route to the aluminum enolates. Nickel-catalyzed conjugate addition of trimethylaluminum to α,β-enones is known,[3] but its efficiency and selectivity are not satisfactory. Conjugate addition of the X group of the organoaluminum compounds R_2AlX (X = SPh,[4] SeMe,[4] C≡CR[5]) has also been reported. Very recently we have reported the methylcopper(MeCu)-catalyzed selective conjugate reduction of α,β-unsaturated carbonyl compounds by diisobutylaluminum hydride (DIBAH) in the presence of a hexamethylphosphoric triamide (HMPA) ligand.[6] The high efficiency of the conjugate reduction indicates the quantitative formation of the aluminum enolates by the hydroalumination of α,β-unsaturated carbonyl compounds with DIBAH–HMPA (eq 1). Thus the MeCu-catalyzed reaction of α,β-unsaturated carbonyl compounds with DIBAH–HMPA offers a convenient method of generating the aluminum enolates. For further utilization of these aluminum enolates in organic synthesis, we have investigated here their reaction with organic halides including trimethylsilyl chloride (eq 1). To our knowledge, the reaction of the aluminum enolates with organic halides has not been reported, while the addition reactions to carbonyl groups are well-documented.[1,2,4]



(1)

Alkylation of the aluminum enolates generated from the MeCu-catalyzed or uncatalyzed reaction of α,β-unsaturated carbonyl compounds and DIBAH–HMPA with alkyl halides did not proceed easily. For example, the aluminum enolate from cyclohexenone failed to react with 5 equiv of allyl bromide at ambient temperature during 2 h and gave 2-allylcyclohexanone only in a low yield (11%) even at the elevated reaction temperature of 50 °C. Now it has been found that conversion of the aluminum enolates into the ate complexes by addition of an equimolar amount of methyllithium (eq 1) increases their nucleophilic reactivity toward alkyl halides to produce alkylated products in moderate to good yields. The results of the alkylation of the ate complexes of aluminum enolates with organic halides are summarized in Table I. Throughout the alkylation reactions in Table I, formation of side alkylation products such as O-alkylated and dialkylated products was not observed in GLC analysis. In addition to allyl bromide, alkyl iodides can be used as alkylating agents (entries 4, 6, 7, and 12). Simple alkyl bromides were inert, although an alkyl bromide activated by a cyano group gave the alkylated product (entry 8). An efficient synthesis of 2-methylcyclopentanone by the usual base-promoted procedures fails because of polyalkylation. A recently reported procedure is highly dependent on the reaction conditions such as base, solvent, and temperature.[7] The present reaction starting from 2-cyclopentenone gave 2-methylcyclopentanone in 59% isolated yield with a trace amount of polyalkylated products (entry 4). The example using carvone shows that the present hydroalumination–alkylation procedure accomplishes the regioselective α,α-dialkylation of a ketone (entry 14). The alkylation of the aluminum dienolates takes place regioselectively at the α-carbon atom. Formation of a γ-alkylated product was not observed. The produced α-alkylated β,γ-unsaturated carbonyl compounds have the *E* configuration almost exclusively (entries 16 and 17). The reactions of unsaturated esters (entries 15 and 17) suggest that the present reductive alkylation reaction is useful as an indirect method of the α-alkylation of saturated esters.[8] The use of organic halides containing a carbonyl group produced dicarbonyl compounds such as 1,4-diketones and γ-keto esters (entries 3, 10, and 11).

The results in Table I (entries 2, 14, and 16) indicate that the MeCu-catalyzed hydroalumination of α,β-(γ,δ)-unsaturated ketones with DIBAH–HMPA provides an efficient procedure of generating regioselectively the more substituted "thermodynamic" aluminum ketone enolate and also the alkylation of these enolates with organic halides offers an indirect method of the regiospecific α-

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[2] Nozaki, H.; Oshima, K.; Takai, K.; Ozawa, S. *Chem. Lett.* **1979**, 379.

[3] Bagnell, L.; Jeffery, E. A.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1975**, *28*, 801.

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[5] Schwartz, J.; Carr, D. B.; Hansen, R. T.; Dayrit, F. M. *J. Org. Chem.* **1980**, *45*, 3053.

[6] (a) Tsuda, T.; Hayashi, T.; Satomi, H.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 537. (b) Tsuda, T.; Kawamoto, T.; Kumamoto, Y.; Saegusa, T. *Synth. Commun.* **1986**, *16*, 639.

[7] Edwards, H. N.; Uycpalek, A. F.; Corbin, N. C.; McChesney, J. D. *Synth. Commun.* **1978**, *8*, 563.

[8] Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194. For the direct α-alkylation of saturated esters, see: (a) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 2318. (b) Cregge, R. J.; Hermann, J. L.; Lee, C. S.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2425.

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Table I. Reaction of Aluminum Enolates with Organic Halides[a]

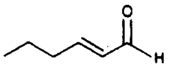
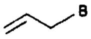
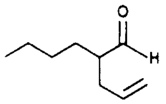
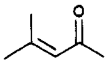
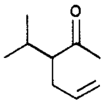
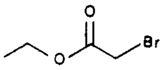
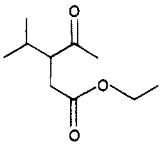
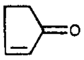
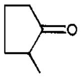
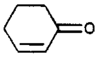
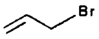
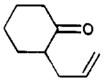
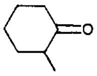
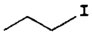
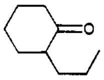
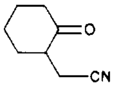
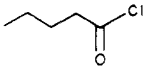
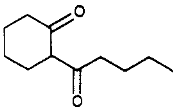
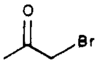
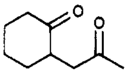
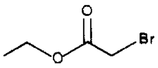
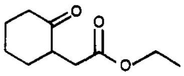
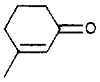
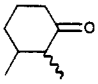
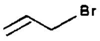
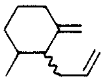
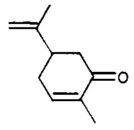
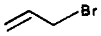
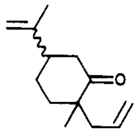
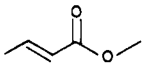
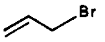
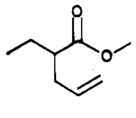
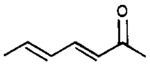
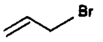
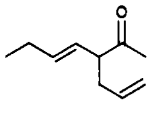
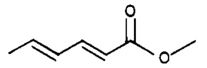
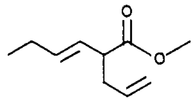
entry	α,β-unsaturated carbonyl compound (S)	RX/S	time, h	product	yield,[c] %
1		 4	2	 **1**	47
2		 4	3.5	 **2**	78
3		 3		 **3**	(77)[d]
4		MeI 3	0.5	 **4**	81 (59)[d]
5		 1.5	2	 **5**	92
6		MeI 1.5	2	 **6**	82
7		 3	2	 **7**	68
8		 4	2	 **8**	40
9		 3	2	 **9**[b]	(80)[d]
10		 2	2	 **10**	40
11		 1.5	2	 **11**	73
12		MeI 3	2	 **12**	71[e]
13		 3	2	 **13**	83 (54)[d]

Table I (Continued)

entry	α,β-unsaturated carbonyl compound (S)	RX/S	time, h	product	yield,[c] %
14		 3	1.5	 **14**	83 (58)[d]
15		 1.5	3.5	 **15**	75
16		 4	3.5	 **16**	77
17		 3	2	 **17**	84 (47)[d]

[a] Reaction was carried out at room temperature. Aluminum enolate was generated in situ by the MeCu (0.10 mmol)-catalyzed hydroalumination of α,β-unsaturated carbonyl compound (S) (1.00 mmol) with DIBAH (1.10 mmol) at −50 °C in THF (5 mL)–HMPA (1 mL) except 2-hexenal, 2-cyclopentenone, and 2-cyclohexenone, the hydroalumination of which were done by the DIBAH–HMPA system alone without MeCu. Aluminum ate complex was formed by the addition of an equimolar amount of MeLi to aluminum. [b] Reaction was carried out at 0 °C. [c] Yield was determined by GLC analysis and was based on α,β-unsaturated compound. [d] Values in parentheses are isolated yields. Reaction for the isolation of product was done using 2.00 mmol of α,β-unsaturated carbonyl compounds and 1.5 equiv of HMPA (0.52 mL) to DIBAH. [e] A mixture of the Z and E isomers, which was separated by GLC using a PEG column (Z/E = 9).

monoalkylation of ketones without polyalkylation. These two features are significant because few procedures[9] that allow the direct regiospecific generation of the "thermodynamic" metal enolates from unsymmetrical ketones are known in comparison with the availability of a variety of procedures for the generation of less substituted "kinetic" enolates and also the alkylation of enolates is known to meet frequently the difficulties such as loss of regioselectivity and formation of polyalkylated products.[10] The reductive alkylation of α,β-unsaturated ketones and esters using LiBH(*sec*-Bu)$_3$ has been reported, where the scope of applicable α,β-unsaturated carbonyl compounds, however, is limited. For example, β-substituted acyclic α,β-enones and β-substituted 2-cyclohexenones undergo the carbonyl reduction. Methyl sorbate is also resistant to the conjugate reduction.

The results of the reaction of the aluminum enolates with trimethylsilyl chloride (Me$_3$SiCl) are summarized in Table II. Me$_3$SiCl reacted with the aluminum enolates themselves without their conversion into the aluminum ate complexes by the addition of methyllithium. It is also noteworthy that a slight excess of Me$_3$SiCl (Me$_3$SiCl/α,β-unsaturated carbonyl compounds = 1.1) is sufficient to effect the quantitative silylation. The aluminum aldehyde enolates generated from cinnamaldehyde and citral were trapped by Me$_3$SiCl to give the corresponding silyl enol ethers in excellent yields. This is significant because control of the generation of the aldehyde enolates is generally difficult.[11] Like the alkylation reaction, the silylation of the aluminum enolates from α,β-enones proceeded in a regiospecific manner to give the more substituted "thermodynamic" trimethylsilyl enol ethers almost quantitatively. Another feature of the present silylation reaction concerns the E,Z stereochemistry around the carbon–carbon double bond of the produced trimethylsilyl enol ethers. As is shown in Table II, the silylation of the acylic aluminum enolates proceeded stereoselectively to produce the thermodynamically more stable silyl enol ethers exclusively or preferably. Thus, the MeCu-catalyzed hydroalumination of α,β-unsaturated carbonyl compounds by DIBAH–HMPA offers another efficient synthetic method of silyl enol ethers from α,β-unsaturated carbonyl compounds.[12]

Experimental Section

IR spectra were determined on a Hitachi 260-50 grating spectrophotometer. ^{1}H NMR spectra were recorded on either a Hitachi R-20B (60 MHz) or JEOL JNM-JX-400 (400 MHz) instrument. ^{13}C NMR spectra were obtained on a Hitachi R-100 spectrometer. All chemical shifts except those of trimethylsilyl enol ethers are reported in parts per million (δ) downfield from internal tetramethylsilane. Chemical shifts of trimethylsilyl enol ethers were obtained on the basis of that of CHCl$_3$ which remains in CDCl$_3$. Mass spectra were obtained on a JEOL DX-300 instrument. Gas chromatographic analyses (GLC) were made on a Schimadzu 4CPT instrument. GLC quantitative analyses of reaction products were made with internal standards with cali-

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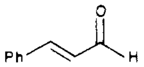
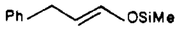
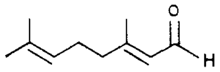
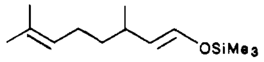
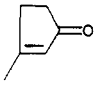
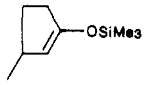
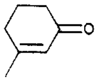
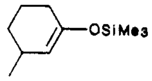
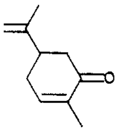
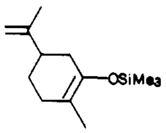
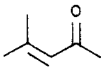
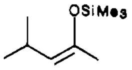
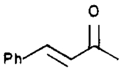
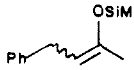
[9] (a) Negishi, E.; Chatterjee, S. *Tetrahedron Lett.* **1983**, *24*, 1341. (b) Kraft, M. E.; Holton, R. A. *Tetrahedron Lett.* **1983**, *24*, 1345.

[10] (a) Jackman, L. M.; Lange, B. C. *Tetrahedron*, **1977**, *33*, 2737. (b) Dangelo, J. *Tetrahedron*, **1976**, *32*, 2979. See also, for example: (c) Liotta, C. L.; Caruso, T. C. *Tetrahedron Lett.* **1985**, *26*, 1599.

[11] For example: Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1982**, 1903.

[12] (a) Brounbridge, P. *Synthesis* **1983**, 1. (b) Rasmussen, J. K. *Synthesis* **1977**, 91. See also: (c) Ojima, I.; Kogure, T. *Tetrahdedron Lett.* **1972**, 5085. (d) Corey, E. J.; Boag, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019. (e) Chamberlin, A. R.; Siegfried, H. R. *J. Am. Chem. Soc.* **1985**, *107*, 1440. (f) Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047.

Table II. Reaction of Aluminum Enolates and Trimethylsilyl Chloride[a]

α,β-unsaturated carbonyl compounds (S)	time (h)	temp. (°C)	trimethylsilyl enol ether (%)[b] (isolated yield)[c]
	3	room temp	 **18** 98 (90)
	3	room temp	 **19** 89 (70)
	3	0	 **20** 98 (70)
	2	0	 **21** 97 (76)
	3	room temp	 **22** 98 (74)
	3	room temp	 **23** 95 (75)[d]
	2	room temp	 **24** 96 (84)[e]

[a] Aluminum enolate was generated in situ by the MeCu (0.10 mmol)-catalyzed hydroalumination of α,β-unsaturated carbonyl compound (2.00 mmol) with DIBAH (2.20 mmol) in THF (5 mL) containing HMPA (3.3 mmol, 0.52 mL) at -50 °C. $Me_3SiCl/S = 1.1$. [b] Determined by GLC. [c] Values in parentheses are isolated yields. [d] Admixed with ca. 10% *E* isomer. [e] *Z* isomer/*E* isomer = 2.6.

bration based upon authentic samples employing a 20% silicone DC 550 on Celite 545 column or a 20% poly(ethylene glycol) (PEG) 20 M on Celite 545 column.

Reactions were carried out under an atmosphere of nitrogen. Cuprous iodide was obtained from Nakarai Chemicals, Ltd., and used without further purification. Diisobutylaluminum hydride (DIBAH) in hexane and methyllithium in ether were obtained from Aldrich Chemical Co. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride under nitrogen. Hexamethylphosphoric triamide (HMPA) was distilled from calcium hydride under reduced pressure. α,β-Unsaturated carbonyl compounds and organic halides were commercial reagents and were distilled under nitrogen after drying over Drierite. Trimethylsilyl chloride was distilled from anhydrous potassium carbonate under nitrogen.

General Procedure for the Reaction of an Aluminum Enolate with an Organic Halide. To a stirred suspension of CuI (190 mg, 0.100 mmol) in 5 mL of THF was added at -10 °C an ether solution of methyllithium (0.100 mmol). HMPA (0.520 mL, 3.00 mmol) and a hexane solution of DIBAH (2.20 mmol) were added successively to the reaction mixture at -50 °C. After being stirred for 0.5 h, the α,β-unsaturated carbonyl compound (2.00 mmol) was added. The mixture was stirred at -50 °C for 1 h and then an ether solution of methyllithium (2.20 mmol) was added. After 0.25 h, the organic halide (6.00 mmol) was added. The mixture was allowed to react at room temperature for the amount of time specified in Table I. To the mixture were added 2 mL of 1 N HCl solution followed by 80 mL of ether. GLC analysis (a silicone DC 550 column) of the ether solution using a hydrocarbon GLC internal standard gave a GLC yield. The separated ether solution was washed twice with 5 mL of 1 N HCl solution and with 5 mL of water, respectively. The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified on a silica gel plate (20 × 20 × 0.2 cm) employing hexane–ether (10:1 v/v) as eluent to give the product.

According to this procedure, ethyl 3-isopropyl-4-oxopentanoate (**3**) (287 mg, 77%), 2-valerylcyclohexanone (**9**) (290 mg, 80%), 2-allyl-3-methylcyclohexanone (**13**) (165 mg, 54%), 2-allyl-2-methyl-4-isopropenylcyclohexanone (**14**) (221 mg, 58%), and methyl 2-allyl-3-hexenoate (**17**) (159 mg, 47%) were isolated and characterized as follows, respectively. **3**: IR (liquid film, cm^{-1}) 1735, 1715; ^1H NMR ($CDCl_3$) δ 0.83 (d, 3 H), 0.97 (d, 3 H), 1.22 (t, 3 H), 1.7–2.2 (m, 1 H), 2.22 (s, 3 H), 2.29 (d, 2 H), 2.6–3.0 (m, 1 H), 4.06 (q, 2 H); mass spectrum (M^+ at *m/e*) 186. **9**: IR (liquid film, cm^{-1}) 1700, 1600; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H), 1.1–1.9 (m, 8 H), 2.1–2.6 (m, 6 H), 16.23 (s, 1 H); mass spectrum (M^+ at *m/e*) 182. **13**: IR (liquid film, cm^{-1}) 1710, 1643; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H), 1.3–2.2 (m, 5 H), 2.2–2.6 (m, 5 H), 4.8–5.2 (m, 2 H), 5.5–6.3 (m, 1 H); mass spectrum (M^+ at *m/e*) 152. **14**: IR (liquid film, cm^{-1}) 1710, 1642; ^1H NMR ($CDCl_3$) δ 1.08 and 1.18 (s, 3 H), 1.78 (s, 3 H), 1.4–2.0 (m, 4 H), 2.2–2.9 (m, 5 H), 4.7–6.1 (m, 5 H); mass spectrum (M^+ at *m/e*) 192. **17**: IR (liquid film, cm^{-1}) 1740, 1640, 970; ^1H NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.8–2.5 (m, 4 H), 2.8–3.1 (m, 1 H), 3.68 (s, 3 H), 4.8–5.9 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.48, 25.48, 36.90, 48.99, 51.68, 116.82, 126.08, 135.38, 174.58; mass spectrum (M^+ at *m/e*) 168.

2-Methylcyclopentanone (**4**) produced by the methylation of the ate complex of the cyclopentanone aluminum enolate, which was generated by the hydroalumination of cyclopentenone with the DIBAH–HMPA system at room temperature, was isolated by Kugelrohr distillation at 52 °C (20 mmHg), and was identified by the agreement of its GLC retention time, IR, and ^1H NMR spectra with those of the commericially available authentic sample.

Similar manipulations using 0.50–1.00 mmol of other α,β-unsaturated carbonyl compounds in THF (5 mL)–HMPA (1 mL) gave the GLC yields of the products shown in Table I. The hydroalumination of 2-hexenal and 2-cyclohexenone was done by the DIBAH–HMPA system alone without MeCu. Each product was isolated by GLC and was identified by the following spectral data except 2-allylcyclohexanone (**5**), 2-methylcyclohexanone (**6**), and 2-propylcyclohexanone (**7**) which were identified by the agreement of their GLC retention times, IR, and/or ^1H NMR spectra with those of the authentic samples. 2-Allylhexanal (**1**): IR (liquid film, cm^{-1}) 1730, 1640; ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H), 1.2–1.8 (m, 6 H), 2.1–2.6 (m, 3 H), 5.0–6.0 (m, 3 H), 9.65 (s, 1 H); mass spectrum (M^+ at *m/e*) 140. 3-Isopropyl-5-hexen-2-one (**2**): IR (liquid film, cm^{-1}) 1710, 1642; ^1H NMR ($CDCl_3$) δ 0.91 (d, 6 H), 1.6–2.0 (m, 1 H), 2.13 (s, 3 H), 2.2–2.5 (m, 3 H), 4.8–6.1 (m, 3 H); mass spectrum (M^+ at *m/e*) 140. 2-(Cyanomethyl)cyclohexanone (**8**): IR (liquid film, cm^{-1}) 2245, 1710; ^1H NMR ($CDCl_3$) δ 1.4–2.1 (m, 6 H), 2.2–2.5 (m, 2 H), 2.64 (d, 2 H), 2.8–3.1 (m, 1 H); mass spectrum (M^+ at *m/e*) 137. 2-Acetonylcyclohexanone (**10**): IR (liquid film, cm^{-1}) 1710; ^1H NMR ($CDCl_3$) δ 1.2–2.0 (m, 6 H), 2.1–2.5 (m, 2 H), 2.22 (s, 3 H), 2.6–3.3 (m, 3 H); mass spectrum (M^+ at *m/e*) 154. 2-[(Ethoxycarbonyl)methyl]cyclohexanone (**11**): IR (liquid film, cm^{-1}) 1740, 1715; ^1H NMR ($CDCl_3$) δ 1.27 (t, 3 H), 1.4–3.0 (11 H), 4.12 (quart, 2 H); mass spectrum (M^+ at *m/e*) 184. (*E*)-2,3-Dimethylcyclohexanone (**12**): IR (liquid film, cm^{-1}) 1710; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 5 Hz, 3 H), 1.09 (d, J = 5 Hz, 3 H), 1.4–2.5 (m, 8 H); mass spectrum (M^+ at *m/e*) 126. (*Z*)-2,3-Dimethylcyclohexanone (**12**): IR (liquid film, cm^{-1}) 1710; ^1H NMR ($CDCl_3$) δ 0.85 (d, J = 9 Hz, 3 H), 0.98 (d, J = 9 Hz, 3 H), 1.5–2.6 (m, 8 H); mass spectrum (M^+ at *m/e*) 126. Methyl 2-ethyl-4-pentenoate (**15**): IR (liquid film, cm^{-1}) 1740, 1640; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.3–1.8 (m, 2 H), 2.1–2.5 (m, 3 H), 3.69 (s, 3 H), 4.8–6.1 (m, 3 H); mass spectrum (M^+ at *m/e*) 142. 2-Allyl-4-hepten-2-one (**16**): IR (liquid film, cm^{-1}) 1720, 1640, 970; ^1H NMR ($CDCl_3$) δ 1.98 (t, 3 H), 2.12 (s, 3 H), 1.6–2.5 (m, 4 H), 3.12 (quart, 1 H), 4.8–6.0 (m, 5 H); ^{13}C NMR ($CDCl_3$) 13.55, 25.65, 28.62, 35.40, 56.86, 116.50, 126.35, 135.76, 136.49, 209.26; mass spectrum (M^+ at *m/e*) 152.

General Procedure of the Reaction of Aluminum Enolate with Trimethylsilyl Chloride. To a stirred suspension of CuI (190 mg, 0.100 mmol) in 5 mL of THF was added at −10 °C an ether solution of methyllithium (0.100 mmol). HMPA (0.52 mL, 3.0 mmol) and a hexane solution of DIBAH (2.20 mmol) were added successively to the reaction mixture at −50 °C. After being stirred for 0.5 h, an α,β-unsaturated carbonyl compound (2.00 mmol) was added. The mixture was stirred at −50 °C for an approporiate reaction time (0.5–3 h). Trimethylsilyl chloride (0.28 mL, 2.2 mmol) was added, and the mixture was allowed to react at room temperature. After the appropriate time, triethylamine (0.29 mL, 2.2 mmol) was added to prevent the hydrolysis of the product of silyl enol ether during the workup. GLC analysis (a silicone DC 550 column) of the mixture using a hydrocarbon GLC internal standard gave a GLC yield. After evaporation of the greater part of THF, silica gel was added to remove inorganic and polar organic materials. The organic residue was chromatographed on silica gel (elution with hexane or pentane) to afford the silyl enol ether product.

According to this procedure, silyl enol ethers **18–24** (Table II) were isolated and identified as follows, respectively. **18**: IR (liquid film, cm^{-1}) 1660, 1595; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 3.24 (d, J = 7.0 Hz, 2 H), 5.24 (d of t, J = 12.2 and 7.0 Hz, 1 H), 6.33 (d, J = 12.2 Hz, 1 H), 7.23 (s, 5 H); mass spectrum (M^+ at *m/e*) 206. **19**: IR (liquid film, cm^{-1}) 1655; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.93 (d, 3 H), 1.1–2.2 (m, 5 H), 1.57 (s, 3 H), 1.66 (s, 3 H), 4.7–5.3 (m, 2 H), 6.15 (d, J = 12.2 Hz, 1 H); mass spectrum (M^+ at *m/e*) 226. **20**: IR (liquid film, cm^{-1}) 1645; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.90 (d, 3 H), 2.0–2.3 (m, 5 H), 4.50 (s, 1 H); mass spectrum (M^+ at *m/e*) 170. **21**: IR (liquid film, cm^{-1}) 1660; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.90 (d, 3 H), 1.5–2.6 (m, 7 H), 4.74 (d, 1 H); mass spectrum (M^+ at *m/e*) 184. **22**: IR (liquid film, cm^{-1}) 1690, 1640; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 1.52 (s, 3 H), 1.69 (s, 3 H), 1.7–2.4 (m, 7 H), 4.68 (s, 2 H); mass spectrum (M^+ at *m/e*) 224. **23**: IR (liquid film, cm^{-1}) 1680; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 0.88 (d, 6 H), 1.71 (s, 3 H), 4.28 (d, 1 H); ^{13}C NMR ($CDCl_3$) 0.61, 22.69, 23.27, 24.80, 116.99, 144.64 ppm; mass spectrum (M^+ at *m/e*) 172. Minor signals that may be assigned to the *E* isomer appear at δ 2.18 (br d) and 4.62 (br d) (^1H NMR) and at 22.4, 23.8, and 25.7 ppm (^{13}C NMR). The approximate ratio of the *Z* isomer to the *E* isomer was 9, which was determined by ^1H NMR. (***Z***)-**24**: IR (liquid film, cm^{-1}) 1670, 1610; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9 H), 1.84 (d, J = 1 Hz, 2 H), 3.35 (d, J = 7 Hz, 2 H), 4.66 (t of quart, J = 7 and 1 Hz, 1 H), 7.14–7.42 (m, 5 H); mass spectrum (M^+ at *m/e*) 220. The ^1H NMR spectra of (*Z*)-**24** was admixed with the signals of the *E* isomer: 3.32 (d, J = 8 Hz, 2 H) and 4.88 (t of quart, J = 8 and 1 Hz, 1 H). The ratio of the *Z* isomer to the *E* isomer was 2.6, which was determined by ^1H NMR of the olefinic protons.

1,4-Dehydrobromination of 1-Bromo-1,2,3-butatrienes: An Efficient Synthesis of 1,4-Disubstituted 1,3-Diynes

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Conjugated diynes are versatile synthetic intermediates[1] and are present in a number of natural products.[2] Here we report an efficient one-pot synthesis of phenyl-substituted conjugated diynes (Scheme I). The key to this approach is the Wittig synthesis of bromo[3]cumulenes **2** (buta-1,2,3-trienes). When treated with an alkoxide base in a protic solvent, these intermediates undergo a novel 1,4-elimination of HBr to form the product diyne **3**.

Phosphacumulene ylides (Scheme I) are established precursors in the preparation of aryl[3] and halogen[4]-substituted [3]cumulenes. Though they are generally unstable, the halo[3]cumulenes can be handled without much difficulty. However, only a few examples have been reported.[5] Our diyne preparation represents the first synthetic utilization of these cumulenes.

The phosphonium salt **1a** was prepared as shown in Scheme II by the bromination of 3-phenylpropynol to yield a 75:25 mixture of isomers **4a** and **4b**. A single recrystallization produced the *E* isomer, **4a**. Treatment of **4a** with triphenylphosphine at room temperature resulted in an 88% yield of **1a**. In the interest of simplicity and economy, the mixture of **4a** and **4b** was converted into isomeric **1b** (*E*/*Z* = 3) which in turn could be used with

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[1] Some of the more recent examples on diacetylene synthesis: Stang, P. J.; Dixit, V. *Synthesis* **1985**, 962. Negishi, E.; Okukado, N.; Lovich, S. F.; Luo, F.-T. *J. Org. Chem.* **1984**, *49*, 2629. Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, *26*, 523. Sinclair, J. A.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 1079. Holmes, A. B.; Jones, G. E. *Tetrahedron Lett.* **1980**, *21*, 3111. Also see: Hunstman, W. D.; In *Chemistry of the Carbon–Carbon Triple Bond* Patai, S., Ed.; Wiley: New York, 1978; Chapter 13.

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[3] Bestmann, H. J.; Schmid, G. *Tetrahedron Lett.* **1975**, 4025. Bestmann, H. J.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 367. Bestmann, H. J.; Saalfrank, R. W.; Snyder, J. P. *Chem. Ber.* **1973**, *106*, 2601. Ratts, K. W.; Partos, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 6112.

[4] Arnold, R. D.; Baldwin, J. E.; Ziegler, C. B., Jr. *J. Chem. Soc., Chem. Commun.* **1984**, 152.

[5] These compounds are air-sensitive and best handled in dilute, argon-degassed CCl_4 solutions. A few examples of known bromo[3]cumulene preparations are the following: Schluback, H. H.; Trautschold, W. *Justus Liebigs Ann. Chem.* **1955**, *594*, 67. Fischer, H.; *Tetrahedron Lett.* **1969**, 435. Other than ref 4, the only example of chloro[3] cumulenes is the parent chlorobutatriene: Vistin, R.; Borg, A.; Lindblom, L. *Acta. Chem. Scand.* **1968**, *22*, 685.

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