237 (35), 207 (25), 191 (22), 178 (32), 165 (45), 115 (40), 91 (35), 77 (28), 63 (25), 39 (20); HRMS calcd for $C_{19}H_{18}O_4$ 310.1205, found 310.1232. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.54; H, 5.81.

3,4-Dimethoxy-7-phenyl-11-oxatricyclo[7.3.0.0^{1,6}]dodeca-2,4,8-trien-10-one (13). A solution of **10** (1.59 g, 4.7 mmol) in dichloroethane (25 mL) was added dropwise to a stirred solution of rhodium(II) octanoate (0.035 g, 0.047 mmol) in dichloroethane (25 mL) heated under reflux in an argon atmosphere. After being heated for an additional 12 h, the solvent was removed under reduced pressure and the residue was recrystallized from hexane to give **13** as a colorless solid: 0.35 g, 17% yield; mp 126–130 °C; IR (CCl_4) 1765, 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37–7.15 (m, 5 H), 6.78 (d, 1 H, J = 1.7 Hz), 4.91 (s, 1 H), 4.72 (d, 1 H, J = 6.7 Hz), 4.34 (d, 1 H, J = 8.7 Hz), 4.29 (dd, 1 H, J = 9.3, 1.7 Hz), 4.14 (d, 1 H, J = 8.7 Hz), 3.69 (s, 3 H), 3.59 (s, 3 H), 2.93 (dd, 1 H, J = 9.3, 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 165.3, 149.2, 149.1, 141.9, 141.7, 140.4, 128.9, 127.5, 127.4, 95.0, 94.1, 82.0, 66.7, 65.8, 57.0, 55.2, 54.6. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.90; H, 6.02. Refluxing of **12** in benzene under argon for 24 h resulted in the formation of **13** in 78% yield.

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Reactivity of Allylic Dimetallic Zinc Reagents. 1

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Allylic 1,1-dimetallic species **2**, prepared in situ from the propargylic ether **1**, are multicoupling reagents. They were allowed to react in a one-pot reaction, with a large variety of electrophiles E_1—carbonyl compounds (acyl chlorides, aldehydes, ketones, phenyl isocyanate, methyl chloroformate), alkyl bromides, and an amino ether—and then E_2—acidic water, iodine, aryl or vinyl iodide in the presence of palladium(0). The isolated yields, based on **1** (5 steps), are fair to good in most cases. The first attack (E_1) always occurs on the carbon atom α to the oxygen; the second attack (E_2) is regio- and stereoselective on the carbon atom α to the TMS moiety.

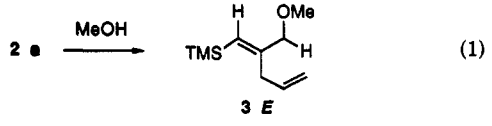
Introduction

Allylic 1,1-dimetallic reagents **2** are potential dicoupling nucleophiles, easily available from 1-(trimethylsilyl)-3-alkoxyprop-1-yne **1** which is first metallated with *n*-butyllithium and then reacted with allylzinc bromide[1] (Scheme I). m_1 and m_2 are not yet clearly defined but may represent two zinc atoms, the species being a dimer.

In a previous paper,[1] we reported the reactivity of the dimetallic species **2a** with benzaldehyde, isobutyraldehyde, acetophenone, and ethyl benzoate as first electrophiles (E_1) and proton as the second one (E_2). We describe herein the extension of this reaction to **1b** with a large variety of carbonyl compounds, with alkyl halides, and with an amino ether. The second electrophile is either acidic water (H_3O^+), iodine, or aryl or vinyl iodide in the presence of palladium(0). In all cases, the reaction is regio- and stereoselective as shown below.

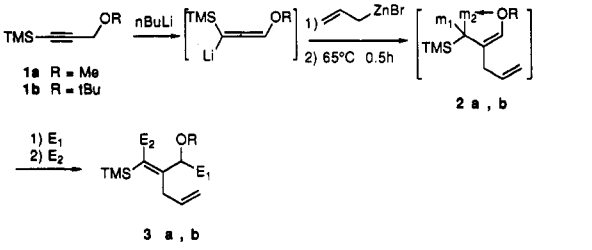
Results and Discussion

(a) Regio- and Stereoselectivity of the Reaction. First, the treatment of **2a** with excess methanol[1] led to a single isomer (**3*E***) (eq 1). Compound **3*E*** has been compared to both ***E*** and ***Z*** authentic samples prepared by other routes[2] described in Scheme II. Concerning the preparation of isomer **3*Z***, it is important to notice that

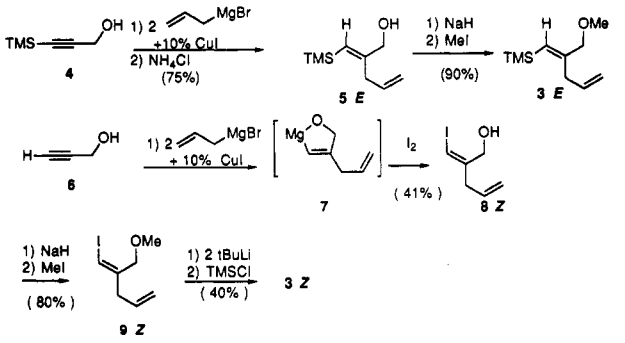


(1)

Scheme I. Synthesis and General Reactivity of Dimetallic Reagents 2



Scheme II. Synthesis of *E* and *Z* Isomers of 3



the supposed intermediate **7** did not react with chlortrimethylsilane to give **5*Z*** in acceptable yield, as previously observed by Jousseaume.[3] Indeed, in compound **7**, the strong chelation of magnesium with the oxygen atom

(1) Normant, J. F.; Quirion, J. C.; Alexakis, A.; Masuda, Y. *Tetrahedron Lett.* **1989**, *30*, 3955.

(2) Duboudin, J. G.; Jousseaume, B. *J. Organomet. Chem.* **1979**, *168*, 1.

(3) Jousseaume, B.; Duboudin, J. G. *J. Organomet. Chem.* **1975**, *91*, C1.

(4) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 1039, 1043, 4427, 4431, 5727.

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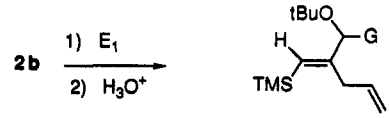
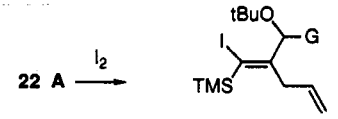
Table I. Reaction of the Dimetallic Species 2b with Various E_1 (E_2 = H_3O^+)



entry	E_1	products, G	no.	isolated yield (%)	ratio[b] of diastereoisomers
1	PhCOCl	COPh	10	78	
2	(*E*)-MeCH=CHCOCl	CO-CH=CHMe-(*E*)	11	64[a]	
3	MeCOMe	$CMe_2(OH)$	12	78	
4	PhCOMe	CMePh(OH)	13	88	1:1
5	H_2C=CHCOMe	$CMe(OH)(CH=CH_2)$	14	60[a]	9:1
6	PhCHO	CH(OH)Ph	15	60[a]	1:1
7	(*E*)-MeCH=CHCHO	CH(OH)(CH=CHMe)-(*E*)	16	63[a]	3:1
8	PhCHO/TMSCl	CHPh(OTMS)	17	60[a]	1:1
9	PhNCO	CONHPh	18	69	
10	ClCOOMe	COOMe	19	68	
11	$BrCH_2Ph$	CH_2Ph	20	70	
12	$BuOCH_2NC_5H_{10}$[c]	$CH_2NC_5H_{10}$[c]	21	33	

[a] Nonoptimized yield. [b] Ratio by GC and/or ^1H NMR. [c] NC_5H_{10} = 1-piperidyl.

Table II. Iodinolysis of Monometallic Reagent 22A



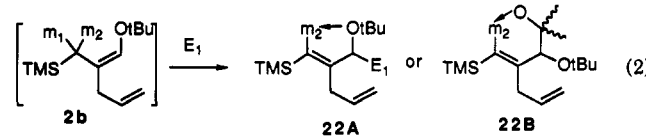
entry	E_1	products, G	no.	isolated yield[c] (%)
1	PhCOCl	COPh	23	78
2	(*E*)-MeCH=CHCOCl	COCH=CHMe-(*E*)	24	67
3	MeCOCl	COMe	25	66
4	EtCOCl	COEt	26	78
5	PhCHO/TMSCl	CHPh(OTMS)	27	63[b]
6	(*E*)-MeCH=CHCHO/TMSCl	CH(CH=CHMe)OTMS (*E*)	28	66[c]
7	PhCOMe/TMSCl	CMePh(OTMS)	29	0[d]
8	Me_2CO/thexMe_2SiCl	CMe_2(OSiMe_2thex)	30	0[d]
9	ClCOOMe	COOMe	31	67
10	PhNCO	CONHPh	32	0[d]
11	CH_2=$CHCH_2Br$	CH_2CH=CH_2	33	50[e]

[a] Based on the propargylic ether 1 (5 steps). [b] Ratio of diastereoisomers 1:1 according to ^1H NMR. The isomers were separable by flash chromatography. [c] Nonoptimized yield; ratio of diastereoisomers 97:3 according to ^1H NMR. [d] Isolated product: proton instead of iodine. [e] Side reactions observed.

causes a loss of nucleophilicity for the vinylic carbon bearing magnesium and consequently inhibits any reaction with most electrophiles except for hydrolysis and iodinolysis. Consequently, the trimethylsilyl residue could only be introduced in the molecule in the last step, after methylation of the hydroxy group in **8** and further halogen–metal exchange from **9**. The regio- and stereoselectivity of this double protonation of **2a** was also observed in the reaction of other electrophiles with **2b**, as described below. The allylic position of the metals in species **2** and a presumed chelation of one of them by the oxygen atom, as shown in Scheme I, are certainly responsible for this selectivity.

(b) Reaction of 2b with Carbonyl Compounds, Alkyl Halides, and an Amino Ether as E_1 with H_3O^+ as E_2. The dimetallic reagent **2b** was chosen instead of **2a** for further investigations since *tert*-butyl ethers are known to be easily cleaved with acetic anhydride in the presence of $FeCl_3$.[5,6] As shown in Table I, **2b** displayed the same regio- and stereoselectivity in the reaction with carbonyl compounds (acyl chlorides, ketones, aldehydes, phenyl isocyanate, methyl chloroformate), alkyl halides (allyl bromide, benzyl bromide), and amino ether. All compounds were obtained in good yields except in case of the amino ether (entry 12). The reaction proceeded fast at low temperature (it started at −80 °C) with carbonyl compounds but required at least 1 day at room temperature for the alkylations. When E_1 is an aldehyde or an unsymmetrical ketone, no or fair diastereoselectivity is observed, despite the presence of the large *tert*-butoxy substituent. However, the reactivity of the gem dimetallic species **2** is totally different from the one observed with nonallylic dimetallic species previously published by Knochel and Normant[4] where the carbonyl olefination was the only outcome.

(c) Reactivity of the Second Metal (m_2). The reaction of the dimetallic species **2** with the first electrophile E_1 led to a monometallic compound **22** (eq 2), which displayed a much lower reactivity than **2**, due to the vinylic position of m_2 and to a presumed chelation of m_2 with an heteroatom belonging either to *O-t*-Bu (**22A**) or to E_1 (**22B**). However, iodinolysis succeeded in good yield only

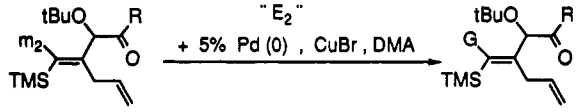


(2)

when solid iodine was rapidly added to the mixture at room temperature. With E_1 = aldehydes, ketones, or phenyl

(5) Alexakis, A.; Gardette, M.; Colin, S. *Tetrahedron Lett.* **1988**, *29*, 2951.
(6) Ganem, B.; Small, V. R., Jr. *J. Org. Chem.* **1974**, *39*, 3728.

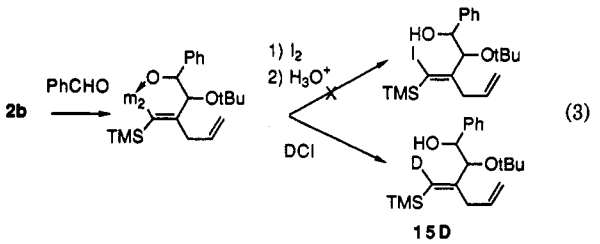
Table III. Coupling Reactions Catalyzed by $Pd(PPh_3)_4$



entry	R	E_2	G	no.	reactn time (h)	isolated yield[a] (%)
1	(*E*)-MeCH=CH	(*E*)-EtCH=CHI	(*E*)-EtCH=CH	**34**	2.5	70
2	(*E*)-MeCH=CH	(*Z*)[10] *t*-BuOOCCH=CHI	(*Z*)-*t*-BuOOCCH=CH	**35**	1.0	51[b]
3	(*E*)-MeCH=CH	*p*-iodoanisole	*p*-MeO-C_6H_4	**36**	4.0	63
4	Ph	(*E*)-EtCH=CHI	(*E*)-EtCH=CH	**37**	2.5	74

[a] Based on the starting propargyl ether **1b** (5 steps). [b] Nonoptimized.

isocyanate, no iodinolysis could be observed. The isolated product was the hydrolyzed one. The metal m_2 is still present as proven by deuterolysis in the case of benzaldehyde (eq 3). To avoid a presumed chelation due to

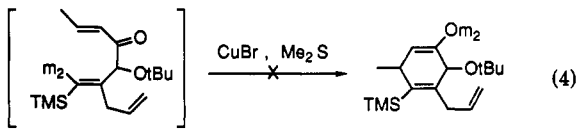


(3)

the alcoholate resulting from E_1, aldehydes and ketones were added with trimethylchlorosilane or thexyldimethylchlorosilane to the dimetallic reagent **2**. With this procedure, the iodinolysis succeeded with aldehydes/TMSCl but failed with ketones. For the latter, silylation of a tertiary alcoholate is not as fast as a that of secondary alcoholate. After workup, the hydrolysis product was the only one identified. The results of iodinolysis are summarized in Table II.

Mono- or disubstituted vinylzinc halides or arylzinc halides are known to couple with alkenyl or arylhalides in the presence of palladium(0) in THF.[7] Under these usual conditions, no reaction occurred with the trisubstituted vinylic substrates of type **22**. To realize an effective coupling, the reaction required not only Pd(0) but also stoichiometric amounts of copper bromide and a cosolvent such as dimethylacetamide (DMA) or DMF.[8,9] The results are summarized in Table III. As indicated in this table, the coupling reactions were carried out in the case of E_1 = acyl chlorides with (*Z*)- or (*E*)-vinyl iodides and an aryl iodide. The yields were fair but not always optimized. The reaction is stereospecific in all cases. It is also worth noting that the yields fell under 5% in the absence of CuBr, although a THF:DMA (3:1) mixture was used, and were about 20% in the presence of CuBr alone, despite a longer reaction time (15 h). $Pd(PPh_3)_4$ or $(Ph_3P)_2PdCl_2$ plus 2 equiv of DIBAL-H afforded similar results, slightly in favor of $Pd(PPh_3)_4$. As expected, the reaction proceeded faster with a vinyl iodide substituted by an electron-withdrawing group (entry 2, Table III).

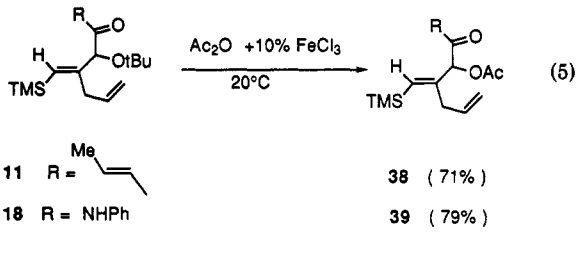
Concerning the reactivity of the second metal, we were unable to protonate a cyclization in the case where E_1 was an α,β-ethylenic acid halide, even in the presence of added copper salts (eq 4). Furthermore, with diacyl chlorides



(4)

such as oxalyl chloride, fumaryl chloride, and malonyl chloride, the reaction of the dimetallic species **2b** occurred fast at low temperature (−80 to −50 °C) but no product except polymers could be isolated after workup.

(d) Cleavage of the *tert*-Butoxy Ether. The cleavage of the *tert*-butoxy ether was realized on two samples, compounds **11** and **18**, according to the literature.[5,6] The corresponding acetoxy products were isolated in good yields (eq 5).



(5)

Conclusion

We have shown that allylic dimetallic zinc reagents of type **2** can react twice, with two different electrophiles: the first attack always occurs on carbon 1 bearing the alkoxy group, and the second attack is regio- and stereoselective on carbon 3. The lower reactivity of the vinylic metallic reagent is responsible for this chemoselectivity. However excellent electrophiles must be used in the second step (I_2, H_2O) but palladium-catalyzed vinylation or arylation occurs efficiently. It should be pointed out that these reactions allow the introduction of three carbon moieties on a propargylic ether in a one-pot reaction.

Experimental Section

THF and diethyl ether were dried over KOH and 4-Å molecular sieves, respectively. Both were then distilled from sodium–benzophenone and stored under nitrogen. All reaction flasks and syringes were oven-dried (130 °C) and the reactions were carried out under N_2.

NMR spectra were recorded on a JEOL FX 90Q, a BRUKER AC 200, or a JEOL GSX 400, in $CDCl_3$ with tetramethylsilane as internal standard. When a TMS moiety was present in the molecule, $CDCl_3$ itself was used as internal standard. IR spectral data are reported in cm^{-1}. Zinc was generously given by the Vieille Montagne Company. *J* values are in hertz.

(7) See, for example: Negishi, E. I. *Acc. Chem. Res.* **1982**, 340 and references cited therein.

(8) Amides have already been used as solvents in Pd(0)-catalyzed reactions of stannanes and zinc reagents; see, for example: (a) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551. (b) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (c) Tamaru, Y.; Ochiai, H.; Sanda, F.; Yoshida, F. *Tetrahedron Lett.* **1985**, *26*, 5529.

(9) For a complete study on these coupling conditions with other substrates and reagents, see: Labaudinière, L.; Normant, J.-F. *Tetrahedron Lett.* **1992**, *33*, 6139.

(10) Ma, S.; Lu, X. *J. Chem. Soc., Chem. Commun.* **1990**, 1643.

Preparation of Allylzinc Bromide.[11] Zinc (4.9 g, 225 mmol) was cut in small pieces (about 0.5 × 0.5 cm) (using gloves) and put in a 100-mL four-necked flask equipped with a mechanic stirrer, a condenser topped with a nitrogen inlet, a thermometer, and a funnel. THF (10 mL) was added just to cover Zn; then a few drops of freshly distilled allyl bromide (4.3 mL, 50 mmol) were added without stirring. The mixture was then brought at 40–50 °C and vigorously stirred, and THF (35 mL) was added. Further addition of allyl bromide was made so that the temperature remained between 25 and 35 °C. Then, the mixture was stirred for about 40 min and filtered while being poured into a dry bottle, under a nitrogen atmosphere, which was closed afterwards with a septum. The solution can be considered as 1 M (±10%) and was kept at −18 °C for 2–3 months.

General Preparation of 1-Methoxy- or 1-*tert*-Butoxy-3-(trimethylsilyl)prop-2-yne (1a,b). A solution of the 1-alkoxyprop-2-yne (535 mmol) in THF (60 mL) was stirred and cooled at −80 °C as *n*-BuLi (1.6 N in hexane, 40 mL) was added. The solution was allowed to warm to 0 °C for 10 min and then cooled to −50 °C for the addition of chlortrimethylsilane (69.45 g, 640 mmol) and further stirred at −50 °C for 30 min. The mixture was hydrolyzed with a saturated NH_4Cl solution and extracted with ether twice (30 mL × 2). After the organic layers were dried ($MgSO_4$), the solvents were removed in vacuo to give an oil which was distilled under reduced pressure giving compound **1a**, bp 79–81 °C (100 mm) (56.50 g, 82%), or **1b**, bp 75 °C (15 mm) (69.82 g, 75%). **1a** ^1H NMR: 3.96 (s, 2 H), 3.25 (s, 3 H), 0.10 (s, 9 H). ^{13}C NMR: 101.5, 91.5, 60.5, 57.6, −0.1. **1b** ^1H NMR: 4.07 (s, 2 H), 1.22 (s, 9 H), 0.15 (s, 9 H). ^{13}C NMR: 103.9, 89.3, 74.3, 51.1, 27.6, −0.1. IR (film): 1245, 1190.

(*E*)-2-[(Trimethylsilyl)methylidene]-4-penten-1-ol (5*E*). A mixture of 3-(trimethylsilyl)prop-2-ynol (2.00 g, 16.0 mmol), diethyl ether (20 mL), and dry copper iodide (0.38 g, 1.6 mmol) was stirred and cooled at −10 °C and allylmagnesium bromide (0.6 N in ether, 67 mL) was added within a few minutes. The reaction was stirred at rt for 2 h and then hydrolyzed at 0 °C with a saturated NH_4Cl solution. The aqueous phase was extracted with 2 × 30 mL portions of ether. The combined organic phases were dried (Na_2SO_4), filtered, and evaporated. The residue was distilled under vacuum, bp 104 °C (10 mm), to give compound **5*E*** (2.04 g, 75%). ^1H NMR: 5.95–5.65 (m, 1 H), 5.58 (br s, 1 H), 5.15–4.90 (m, 2 H), 4.00 (br s, 2 H), 3.20–3.10 (m, 1 H), 3.00 (br s, 1 H), 2.90–2.80 (m, 1 H), 0.10 (s, 9 H). ^{13}C NMR: 154.8, 136.2, 123.1, 116.1, 66.4, 37.3, 0.1. IR (film): 3500–3100.

(*E*)-1-Methoxy-2-[(trimethylsilyl)methylidene]-4-pentene (3*E*). To sodium hydride (0.54 g, 13 mmol) washed twice with ether was added a solution of methyl iodide (6.4 mL, 45 mmol) in THF (10 mL)). Pure alcohol **5*E*** (1.70 g, 10 mmol) was slowly added at 45 °C to the stirred suspension. The mixture was stirred for 10 h at this temperature, hydrolyzed at 0 °C with a saturated NH_4Cl solution, and extracted with 2 × 30 mL portions of ether. The combined extracts were dried (Na_2SO_4), filtered, and evaporated. The residue was distilled (bulb-to-bulb) under reduced pressure (20 mm) to give ether **3*E*** (1.66 g, 90%). ^1H NMR: 5.90–5.58 (m, 1 H), 5.63 (s, 1 H), 5.20–4.95 (m, 2 H), 3.82 (br s, 2 H), 3.33 (s, 3 H), 2.98–2.87 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR: 152.0, 136.2, 126.0, 116.1, 76.9, 58.0, 37.4, 0.3. IR (film): 1248, 1105. Anal. Calcd for $C_{10}H_{19}OSi$: C, 65.28; H, 10.95. Found: C, 65.33; H, 10.87.

(*Z*)-2-(Iodomethylidene)-4-penten-1-ol (8*Z*). A suspension of dry copper iodide (1.34 g, 70 mmol) in a solution of propyn-2-ol (3.90 g, 70 mmol) in diethyl ether (50 mL) was vigorously stirred and cooled at −10 °C as 0.7 N allylmagnesium bromide in ether (250 mL, 175 mmol) was added. After completion of the addition, the mixture was stirred for 2 h at rt. I_2 (24.00 g, 95 mmol) was then added at −60 °C and the mixture was allowed to warm to rt. After 0.5 h, it was cooled to 0 °C, extracted with a saturated sodium thiosulfate solution, and extracted with ether (2 × 50 mL). The organic phases were dried over Na_2SO_4, filtered, and evaporated. The residue was purified by flash chromatography on a silica gel column with cyclohexane:ethyl acetate 4:1 as eluent. Alcohol **8*Z*** (6.43 g, 41%) was obtained as an oil. ^1H NMR: 6.05 (s, 1 H), 5.90–5.70 (m, 1 H), 5.20–5.00 (m, 2 H), 4.25 (s, 2 H), 3.35 (br s, 1 H), 3.10–3.00 (m, 2 H). ^{13}C NMR: 147.8, 134.4, 117.3, 77.1, 66.4, 39.2. IR (film): 3600–3100.

(*Z*)-1-Methoxy-2-(iodomethylidene)-4-pentene (9*Z*). The same procedure as for **3*E*** from alcohol **5*E*** was followed. Compound **9*Z*** (5.14 g, 80%) was obtained from **8*Z*** (6.05 g, 27 mmol). ^1H NMR: 6.15 (s, 1 H), 5.90–5.65 (m, 1 H), 5.15–5.05 (m, 2 H), 4.05 (s, 2 H), 3.30 (s, 3 H), 3.00–2.90 (m, 2 H). ^{13}C NMR: 146.3, 134.6, 117.4, 78.2, 75.7, 58.0, 39.5. Anal. Calcd for $C_7H_{11}IO$: C, 35.33; H, 4.66. Found: C, 35.39; H, 4.72.

(*E*)-1-Methoxy-3-[(trimethylsilyl)methylidene]-4-pentene (3*Z*). *tert*-Butyllithium (1.7 N) in pentane (5.5 mL, 9.4 mmol) was added to iodopropene **9** (1.12 g, 4.7 mmol) in THF (20 mL). The temperature was raised to 0 °C for 30 min and then chlortrimethylsilane (1.5 mL, 9.4 mmol) was added at −80 °C. The reaction was fast and exothermic. Hydrolysis of the mixture was performed at 0 °C with a saturated NH_4Cl solution. After the usual workup, the residue was purified under reduced pressure (20 mm) by bulb-to-bulb distillation to give **3*Z*** (0.69 g, 80%) as an oil. ^1H NMR: 5.90–5.70 (m, 1 H), 5.48 (s, 1 H), 5.05–4.95 (m, 2 H), 3.90 (s, 2 H), 3.30 (s, 3 H), 2.85–2.70 (m, 2 H), 0.10 (s, 9 H). ^{13}C NMR: 153.4, 136.2, 128.8, 116.4, 74.0, 57.7, 41.6, 0.56. Anal. Calcd for $C_{10}H_{19}SiO$: C, 65.28; H, 10.95. Found: C, 65.22; H, 10.90.

General Procedure for the Preparation of the Dimetallic Species 2 and Its Reaction in Situ with Electrophiles. A solution of 1-alkoxy-3-(trimethylsilyl)prop-2-yne (1) (5 mmol) in THF (15 mL) was placed in a 100-mL four-necked flask equipped with a mechanical stirrer, a condenser topped with a nitrogen inlet, a thermometer, and a septum. *n*-BuLi (1.2 equiv) in hexane was added with a syringe at −80 °C and the mixture was stirred for 0.5 h at this temperature (the metalation was checked in GC after an aliquot was quenched with a few drops of pivalaldehyde in dry ether and subsequent hydrolysis with 1 N HCl). Allylzinc bromide (1.2 equiv) was added with a syringe at −80 to −60 °C. The yellow solution became colorless. The mixture was allowed to warm up to 0 °C and was then refluxed for 0.5 h. The organometallic species **2** was formed (this could also be checked by GC after 1 N HCl hydrolysis of an aliquot).

(a) Reaction with Methanol. Methanol (0.5 mL) was added to the mixture, which was cooled to 0 °C, and then stirred and warmed to rt. After hydrolysis with 1 N HCl and extraction with ether, the organic phase was stirred at least for 2 h with several crystals of sodium sulfide hydrate. Without this treatment, small quantities of zinc salts remained in the crude mixture, so that the yields dropped dramatically. The organic phase was washed twice with brine, dried over $MgSO_4$, and evaporated to give an oil, which was bulb-to-bulb distilled to give **3*E*** (0.83 g, 90%).

(b) Reactions with Other Electrophiles E_1. The mixture was cooled to −80 °C and a carbonyl compound (7 mmol) in ether (2 mL) was added with a syringe. In the case of aldehydes, TMSCl (7 mmol) was simultaneously added (entry 8, Table I). For alkyl halides or the amino ether, the reaction was run at −40 °C. After being warmed to rt, the mixture was treated exactly as described in (a) with methanol, except for aldehyde/TMSCl which required a smoother hydrolysis with a saturated NH_4Cl solution instead of 1 N HCl. Flash chromatography columns were eluted with cyclohexane:ethyl acetate 100:0 to 80:20 according to the polarity of the expected product. Yields are given in Table I.

(*E*)-1-Phenyl-2-*tert*-butoxy-3-[(trimethylsilyl)methylidene]-5-hexenone (10). ^1H NMR: 8.40–7.50 (m, 5 H), 6.25 (s, 1 H), 6.15–5.80 (m, 1 H), 5.45–5.20 (m, 2 H), 5.18 (s, 1 H), 3.40–2.95 (m, 2 H), 1.37 (s, 9 H), 0.31 (s, 9 H). ^{13}C NMR: 200.4, 151.8, 136.2, 135.7, 132.6, 129.9, 127.9, 127.8, 116.7, 80.9, 75.9, 36.7, 28.2, −0.1. IR (film): 1680. Anal. Calcd for $C_{20}H_{30}O_2Si$: C, 72.79; H, 9.16. Found: C, 72.85; H, 9.11. CIMS: m/z 349 ($M + H^+ + NH_4^+$, 59), 348 ($M + NH_4^+$, 57), 331 ($M + H^+$, 100).

(*E*,*E*)-5-*tert*-Butoxy-4-[(trimethylsilyl)methylidene]-1,7-nonadien-6-one (11). ^1H NMR: 6.90 (dq, ^3J = 15.4, ^4J = 1.7, 1 H), 6.50 (dq, ^3J = 15.4, ^4J = 1.7, 1 H), 5.92 (d, ^4J = 1.3, 1 H), 5.80–5.69 (m, 1 H), 5.12–5.04 (m, 2 H), 4.35 (d, ^4J = 1.3, 1 H), 2.99 (ddt, ^2J = 15.2, ^3J = 5.5, ^4J = 1.7, 1 H), 2.79 (dd, ^2J = 15.2, ^3J = 15.2, ^3J = 7.2, 1 H), 1.86 (dd, ^3J = 6.6, ^4J = 1.7, 3 H), 1.14 (s, 9 H), 0.10 (s, 9 H). ^{13}C NMR: 200.1, 151.3, 143.0, 136.3, 127.5, 126.6, 116.9, 80.4, 75.7, 36.8, 28.4, 18.5, 0.3. IR (film): 1722, 1688, 1625. Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.45; H, 10.28. Found: C, 69.39; H, 10.33. CIMS: m/z 313 ($M + H^+ + NH_4^+$, 53), 312 ($M + NH_4^+$, 74), 295 ($M + H^+$, 100).

(11) Modified preparation of the method published by Gaudemar, M. *Bull. Soc. Chim. France* **1962**, 974.

(*E*)-2-Methyl-3-*tert*-butoxy-4-[(trimethylsilyl)methylidene]-6-hepten-2-ol (12). ^{1}H NMR: 5.84–5.74 (m, 1 H), 5.67 (s, 1 H), 5.07 (d, ^3J = 17.0, 1 H), 5.02 (d, ^2J = 10.4, 1 H), 3.70 (s, 1 H), 3.14 (dd, ^2J = 14.0, ^3J = 5.0, 1 H), 2.90 (dd, ^2J = 14.0, ^3J = 7.7, 1 H), 2.50 (s, 1 H), 1.19 and 1.07 (2 s, 3 H), 1.12 (s, 9 H), 0.32 (s, 9 H). ^{13}C NMR: 156.2, 138.4, 129.0, 116.2, 75.1, 72.6, 70.5, 39.3, 28.9, 28.4, 0.3. IR (film): 3560, 3450. Anal. Calcd for $C_{16}H_{12}O_2Si$: C, 67.67; H, 11.35. Found: C, 67.60; H, 11.42.

(*E*)-2-Phenyl-3-*tert*-butoxy-4-[(trimethylsilyl)methylidene]-6-hepten-2-ol (13). ^{1}H NMR: 7.60–7.10 (m, 5 H), 5.80 (s, 1 H), 5.85–5.40 (m, 1 H), 5.15–4.70 (m, 2 H), 4.02 and 3.98 (2 s, 1 H), 3.05–2.60 (m, 2 H), 1.60 and 1.45 (2 s, 3 H), 1.12 and 1.00 (2 s, 9 H), 0.12 and 0.02 (2 s, 9 H). The diastereoisomers were in a 1:1 ratio according to signals at 1.60 and 1.45 ppm and at 1.12 and 1.00 ppm. ^{13}C NMR: 155.7, 146.8 and 145.8, 137.9 and 137.8, 129.1, 127.8, 127.4, 126.8 and 126.6, 126.3, 116.2, 81.2 and 80.0, 76.2 and 75.1, 75.8 and 75.5, 39.5, 28.7, 25.7 and 24.3, 0.2. CIMS: m/z 364 (M + NH_4^+, 48), 329 (M + H^+ – H_2O, 100).

(*E*)-3-Methyl-4-*tert*-butoxy-5-[(trimethylsilyl)methylidene]-1,7-octadien-3-ol (14). ^{1}H NMR: 5.90 (dd, ^2J = 14.6, ^2J = 6.6, 1 H), 5.80–5.66 (m, 1 H), 5.68 (s, 1 H), 5.21–4.96 (m, 4 H), 3.80 and 3.77 (2 s, 1 H), 3.15–2.86 (m, 2 H), 2.60 (s, 1 H), 1.22 and 1.19 (2 s, 3 H), 1.19 and 1.18 (2 s, 9 H), 0.11 (s, 9 H). The diastereoisomers were in a more than 9:1 ratio according to signals at 3.80 and 3.77 ppm. ^{13}C NMR: 155.6, 142.6, 138.2, 129.3, 116.3, 112.3, 81.1, 75.2, 74.8, 39.6, 28.9, 25.4, 0.3. The second diastereoisomer did not appear. IR (film): 3540, 3450. CIMS: m/z 314 (M + NH_4^+, 29), 279 (M + H^+ – H_2O, 85), 223 (M + H^+ – t-BuOH, 100).

(*E*)-1-Phenyl-2-*tert*-butoxy-3-[(trimethylsilyl)methylidene]-5-hexen-1-ol (15). ^{1}H NMR: 7.30–7.13 (m, 5 H), 5.90–5.60 (m, 1 H), 5.57 and 5.50 (2 s, 1 H), 5.15–4.90 (m, 2 H), 4.53 and 4.40 (2 d, ^3J = 5.9 and 6.2, respectively, 1 H), 4.00 and 3.95 (2 d, ^3J = 6.1 and 6.2 respectively, 1 H), 3.13 and 2.50 (2 br s, 1 H), 3.00–2.80 (m, 1 H), 2.73 (dd, ^2J = 14.4, ^3J = 8.2, 0.5 H), 2.35 (dd, ^2J = 14.4, ^3J = 8.2, 0.5 H), 1.07 and 0.99 (2 s, 9 H), 0.15 and 0.10 (2 s, 9 H). In the case of **15D** (deuterolysis with CH_3COCl + D_2O), the signals at 5.57 and 5.50 disappeared. ^{13}C NMR: 155.4 and 154.9, 141.1, 137.7 and 137.2, 129.6 and 129.5, 129.4, 128.0, 127.5, 116.8 and 116.5, 81.2 and 80.8, 76.5 and 76.3, 75.5 and 75.0, 38.7 and 37.8, 28.7 and 28.4, 0.21. IR (film): 3600–3200. CIMS: m/z 351 (M + H^+ + NH_4^+, 24), 333 (M + H^+, 16), 315 (M – H_2O + H^+, 41), 259 (M + H^+ – t-BuOH, 71), 169 (M + H^+ – PhCHOH – t-BuH, 100).

(*E*,*E*)-5-*tert*-Butoxy-4-[(trimethylsilyl)methylidene]-1,7-nonadien-6-ol (16). ^{1}H NMR: 5.75–5.60 (m, 1 H), 5.55 (s, 1 H), 5.52–5.40 (dq, ^3J = 14.5, J = 6.4, 1 H), 5.35–5.25 (m, 1 H), 5.05–4.85 (m, 3 H), 3.90–3.80 (m, 1 H), 3.00–2.60 (m, 2 H), 2.18 (br s, 1 H), 1.70 (m, 3 H), 1.25 and 1.15 (2 s, 9 H), 0.15 and 0.05 (2 s, 9 H); ratio of diastereoisomers about 3:1 according to signals at 1.25 and 1.15 ppm. ^{13}C NMR: major diastereoisomer 154.8, 137.1, 130.4, 127.6, 127.2, 116.5, 78.7, 74.7, 73.0, 38.0, 28.7, 17.6, 0.2; minor diastereoisomer 155.2, 137.4, 130.3, 127.9, 127.6, 116.4, 80.4, 75.2, 74.2, 37.9, 28.6, 17.7, 0.2. IR (film): 3540, 3450.

(*E*)-1-Phenyl-1-[(trimethylsilyl)oxy]-2-*tert*-butoxy-3-[(trimethylsilyl)methylidene]-5-hexene (17). Attribution of signals for both diastereoisomers (ratio about 1:1) was confirmed by NMR CH COSY. **First Isomer.** ^{1}H NMR: 7.50–7.25 (m, 5 H), 6.15–5.90 (m, 1 H), 5.85 (s, 1 H), 5.40–5.10 (m, 2 H), 4.55 (d, ^3J = 6.5, 1 H), 4.00 (d, ^3J = 6.5, 1 H), 3.25 (br d, ^2J = 5.9, 2 H), 0.95 (s, 9 H), 0.25 (s, 9 H), 0.10 (s, 9 H). ^{13}C NMR: 158.2, 144.2, 138.5, 128.0, 127.4, 127.1, 125.9, 116.1, 79.6, 79.5, 74.5, 40.1, 28.4, 0.6, 0.3. **Second Isomer.** ^{1}H NMR: 7.50–7.18 (m, 5 H), 5.82–5.73 (m, 2 H), 5.14 (br d, ^3J = 17.4, 1 H), 5.02 (br d, ^3J = 9.9, 1 H), 4.82 (d, ^3J = 3.9, 1 H), 4.65 (d, ^3J = 3.9, 1 H), 3.41 (dd, ^2J = 15.4, ^3J = 7.7, 1 H), 3.18 (br dd, ^2J = 15.4, ^3J = 2.2, 1 H), 0.85 (s, 9 H), 0.28 (s, 9 H), 0.01 (s, 9 H). ^{13}C NMR: 157.6, 142.4, 139.4, 127.6, 127.3, 127.0, 115.5, 111.2, 86.9, 77.3, 75.0, 37.1, 27.9, 1.9, 0.2. CIMS: m/z 350 (M + NH_4^+ – TMS, 59), 169 (M – PhCHOTMS – t-Bu, 100).

(*E*)-*N*-Phenyl-2-*tert*-butoxy-3-[(trimethylsilyl)methylidene]-5-hexenamide (18). ^{1}H NMR: 8.45 (br s, 1 H), 7.58–7.08 (m, 5 H), 5.85 (d, ^4J = 1.1, 1 H), 5.83–5.73 (m, 1 H), 5.15 (br dd, ^3J = 17.1, ^2J = 1.7, 1 H), 5.04 (dd, ^3J = 9.9, ^2J = 1.1, 1 H), 4.45 (d, ^4J = 1.1, 1 H), 3.23 (dd, ^2J = 14.8, ^3J = 7.7, 1 H), 3.05 (ddt, ^2J = 12.9, ^3J = 5.5, ^4J = 1.7, 1 H), 1.15 (s, 1 H), 0.12 (s, 9 H). ^{13}C NMR: 170.4, 152.6, 137.7, 136.6, 129.1, 127.9, 124.3, 119.6, 116.9, 76.7, 76.6, 37.2, 28.3, 0.2. IR (Nujol): 3380, 3350, 1678, 1600, 1460, 1435. CIMS: m/z 363 (M + NH_4^+, 4), 346 (M + H^+, 100).

(*E*)-Methyl 2-*tert*-Butoxy-3-[(trimethylsilyl)methylidene]-5-hexenoate (19). ^{1}H NMR: 5.76 (s, 1 H), 5.76–5.70 (m, 1 H), 5.13–5.02 (m, 2 H), 4.48 (s, 1 H), 3.70 (s, 3 H), 4.05–3.85 (m, 2 H), 1.17 (s, 9 H), 0.10 (s, 9 H). ^{13}C NMR: 173.1, 150.5, 136.2, 127.9, 116.5, 75.6, 74.9, 51.9, 36.7, 27.8, 0.1. IR (film): 1755, 1730, 1612. Anal. Calcd: C, 63.34; H, 9.92. Found: C, 63.31; H, 9.90. CIMS: m/z 302 (M + NH_4^+, 100), 246 (M – t-Bu, 46).

(*E*)-1-Phenyl-2-*tert*-butoxy-3-[(trimethylsilyl)methylidene]-5-hexene (20). ^{1}H NMR: 7.30–7.10 (m, 5 H), 5.95–5.75 (m, 1 H), 5.55 (s, 1 H), 5.25–5.05 (m, 1 H), 3.93 (dd, ^3J = 8.7, ^3J = 3.4, 1 H), 3.11–2.85 (m, 2 H), 2.79 (dd, ^2J = 13.5, ^3J = 4.0, 1 H), 2.51 (dd, ^2J = 13.5, ^3J = 8.7, 1 H), 0.75 (s, 9 H), 0.10 (s, 9 H). ^{13}C NMR: 158.3, 140.3, 137.8, 130.1, 127.9, 126.0, 124.5, 116.4, 77.6, 74.2, 43.8, 38.3, 28.4, 0.44. Anal. Calcd: C, 75.07; H, 10.61. Found: C, 75.14; H, 10.69.

(*E*)-2-*tert*-Butoxy-3-[(trimethylsilyl)methylidene]-1-piperidino-5-hexene (21). ^{1}H NMR: 5.90–5.65 (m, 1 H), 5.70 (s, 1 H), 5.15–4.95 (m, 2 H), 4.02 (t, ^3J = 6.0, 1 H), 3.10–2.85 (m, 2 H), 2.60–2.30 (m, 4 H), 2.25 (d, ^3J = 6.0, 2 H), 1.60–1.45 (m, 6 H), 1.10 (s, 9 H), 0.11 (s, 9 H). ^{13}C NMR: 158.3, 137.9, 124.5, 115.9, 75.8, 74.3, 65.3, 55.4, 38.1, 28.8, 26.3, 24.6, 0.1.

Reaction of the Vinylic Species 22 with Iodine: General Procedure. After reaction with the first electrophile and then warming to rt, 5 mmol (1 equiv) solid iodine was added to the vigorously stirred mixture. The reaction was about 10 °C exothermic and remained dark. The mixture was then hydrolyzed with 1 N HCl or a saturated NH_4Cl solution in the presence of sodium thiosulfate. The organic phase was stirred at least for 2 h with several crystals of sodium sulfide hydrate, washed twice with brine, dried ($MgSO_4$), and evaporated to give an oil. The same eluents as above (for compounds of Table I) were also used for the flash chromatography. Yields are given in Table II.

(*Z*)-1-Phenyl-2-*tert*-butoxy-3-[iodo(trimethylsilyl)methylidene]-5-hexen-1-one (23). ^{1}H NMR: 7.78–7.72 (m, 2 H), 7.30–7.10 (m, 3 H), 5.89 (s, 1 H), 5.59–5.48 (m, 1 H), 4.58–4.52 (m, 2 H), 3.26 (dd, ^2J = 15.0, ^3J = 8.0, 1 H), 3.12 (dd, ^2J = 15.0, ^3J = 5.3, 1 H), 1.24 (s, 9 H), 0.26 (s, 9 H). ^{13}C NMR: 199.6, 152.5, 137.1, 136.4, 132.6, 129.2, 128.1, 116.4, 115.9, 86.6, 76.1, 47.8, 28.9, 1.8. IR (film): 1720, 1690, 1632, 1595. CIMS: m/z = 474 (M + NH_4^+, 59), 457 (M + H^+, 100).

(*Z*,*E*)-5-*tert*-Butoxy-4-[iodo(trimethylsilyl)methylidene]-1,7-nonadien-6-one (24). ^{1}H NMR: 6.89 (dd, ^3J = 15.4, ^3J = 7.2, 1 H), 6.63 (dd, ^3J = 15.4, ^4J = 1.7, 1 H), 5.59–5.49 (m, 1 H), 5.30 (s, 1 H), 4.96 (dd, ^3J = 17.0, ^2J = 1.4, 1 H), 4.88 (dd, ^3J = 9.9, ^2J = 1.4, 1 H), 3.17 (dd, ^3J = 15.4, ^3J = 7.3, 1 H), 3.04 (dd, ^3J = 15.4, ^3J = 5.2, 1 H), 1.85 (dd, ^3J = 7.2, ^4J = 1.7, 3 H), 1.22 (s, 9 H), 0.30 (s, 9 H). ^{13}C NMR: 196.6, 156.0, 143.0, 135.9, 127.2, 114.4, 116.8, 88.3, 75.9, 36.1, 28.4, 18.4, 1.9. IR (film): 1725, 1700, 1630, 1245. CIMS: m/z 438 (M + NH_4^+, 40), 421 (M + H^+, 96), 365 (M – C_4H_8, 100).

(*Z*)-3-*tert*-Butoxy-4-[iodo(trimethylsilyl)methylidene]-6-hepten-2-one (25). ^{1}H NMR: 5.58–5.47 (m, 1 H), 5.15 (s, 1 H), 5.02 (dd, ^3J = 17.0, ^2J = 1.1, 1 H), 4.93 (dd, ^3J = 9.9, ^2J = 1.1, 1 H), 2.87 (dd, ^2J = 14.7, ^3J = 8.3, 1 H), 2.77 (dd, ^2J = 14.7, ^3J = 5.3), 2.14 (s, 3 H), 1.20 (s, 9 H), 0.30 (s, 9 H). ^{13}C NMR: 207.0, 154.2, 135.7, 117.4, 114.4, 89.1, 76.1, 42.7, 28.4, 27.6, 2.0. IR (film): 1725, 1633, 1245, 1083. CIMS: m/z 412 (M + NH_4^+, 91), 395 (M + H^+, 100).

(*Z*)-3-*tert*-Butoxy-4-[iodo(trimethylsilyl)methylidene]-1-octen-6-one (26). ^{1}H NMR: 5.55–5.45 (m, 1 H), 5.20 (s, 1 H), 4.97 (dd, ^3J = 17.0, ^2J = 1.1, 1 H), 4.91 (dd, ^3J = 9.9, ^2J = 1.1, 1 H), 3.17 (dd, ^2J = 14.9, ^3J = 7.7, 1 H), 3.00 (dd, ^2J = 14.9, ^3J = 4.9, 1 H), 2.64 (dt, ^2J = 19.0, ^3J = 7.2, 1 H), 2.44 (dt, ^2J = 19.0, ^3J = 7.2, 1 H), 1.20 (s, 9 H), 0.95 (t, ^3J = 7.2, 3 H), 0.30 (s, 9 H). ^{13}C NMR: 209.0, 154.6, 135.8, 116.9, 114.1, 88.7, 76.0, 36.4, 32.7, 28.4, 7.6, 2.0. IR (film): 1715, 1245, 1085. CIMS: m/z 426 (M + NH_4^+, 83), 409 (M + H^+, 100).

(*Z*)-1-Phenyl-1-[(trimethylsilyl)oxy]-2-*tert*-butoxy-3-[iodo(trimethylsilyl)methylidene]-5-hexene (27). First Diastereoisomer (Less Polar). ^{1}H NMR: 7.60–7.55 (m, 2 H), 7.45–7.33 (m, 3 H), 6.01–5.90 (m, 1 H), 5.31 (dd, ^3J = 17.1, ^2J = 1.7, 1 H), 5.17 (dd, ^3J = 10.5, ^2J = 1.7, 1 H), 4.90 (d, ^3J = 8.0, 1

H), 4.58 (d, ^3J = 8.0, 1 H), 3.43 (ddd, ^2J = 15.4, ^3J = 6.1, ^4J = 1.7, 1 H), 3.23 (ddd, ^2J = 15.4, ^3J = 6.1, ^4J = 1.7, 1 H), 1.03 (s, 9 H), 0.47 (s, 9 H), 0.15 (s, 9 H). ^{13}C NMR: 155.9, 143.9, 138.8, 128.7, 127.6, 116.0, 87.9, 77.3, 75.1, 36.1, 28.2, 2.4, 0.7. CIMS: m/z 549 (M + NH_4^+, 2), 531 (M + H^+, 4), 441 (M + H^+ - TMSOH, 100), 367 (M + H^+ - TMSOH - t-BuOH, 14). **Second Diastereoisomer.** ^{1}H NMR: 7.65–7.40 (m, 2 H), 7.53–7.38 (m, 3 H), 6.02–5.90 (m, 1 H), 5.33 (dd, ^3J = 17.1, ^2J = 1.1, 1 H), 5.23 (dd, ^3J = 11.0, ^2J = 1.1, 1 H), 5.02 (d, ^3J = 3.9, 1 H), 4.84 (d, ^3J = 3.9, 1 H), 3.61 (dd, ^2J = 15.4, ^3J = 7.7, 1 H), 3.39 (dddd, ^2J = 15.4, ^3J = 4.4, ^4J = 2.3, ^4J = 2.2, 1 H), 1.05 (s, 9 H), 0.48 (s, 9 H), 0.18 (s, 9 H). ^{13}C NMR: 157.5, 142.4, 139.4, 127.6, 127.4, 127.2, 117.0, 86.9, 77.3, 75.0, 37.1, 27.9, 1.9, 0.3. Structures were confirmed by NMR CH COSY. CIMS: m/z 549 (M + NH_4^+, 9), 5.31 (M + H^+, 34), 441 (M + H^+ - TMSOH, 90), 367 (M + H^+ - TMSOH - t-BuOH, 100).

(*Z*,*E*)-5-*tert*-Butoxy-6-[(trimethylsilyl)oxy]-4-[iodo(trimethylsilyl)methylidene]-1,7-nonadiene (28). ^{1}H NMR: 5.78–5.68 (m, 1 H), 5.58–5.45 (m, 2 H), 5.07 (dd, ^3J = 17.6, ^2J = 1.6, 1 H), 4.97 (dd, ^3J = 10.2, ^2J = 1.6, 1 H), 4.58 (d, ^3J = 6.6, 1 H), 3.93 (dd, ^3J = 7.2, ^3J = 6.6, 1 H), 3.20 (ddd, ^2J = 15.4, ^3J = 6.1, ^3J = 1.7), 3.10 (ddd, ^2J = 15.4, ^3J = 6.1, ^3J = 1.7), 1.58 (d, ^3J = 5.0, 3 H), 1.12 (s, 9 H), 0.30 (s, 9 H), 0.05 (s, 9 H). ^{13}C NMR: 156.0, 138.9, 133.2, 127.2, 115.4, 112.9, 85.9, 75.9, 75.1, 36.0, 28.6, 17.8, 2.0, 1.0. Anal. Calcd: C, 48.57; H, 7.95. Found: C, 48.75; H, 8.02. CIMS: m/z 405 (M + H^+ - TMSOH, 64), 351 (M + H^+ - $CH_3CH{=}CHCH_2OTMS$, 100).

(*Z*)-Methyl 2-*tert*-Butoxy-3-[iodo(trimethylsilyl)methylidene]-5-hexenoate (31). ^{1}H NMR: 5.71–5.60 (m, 1 H), 5.32 (s, 1 H), 5.03–4.95 (m, 2 H), 3.63 (s, 3 H), 3.27 (ddt, ^2J = 14.3, ^3J = 8.8, ^4J = 1.7, 1 H), 3.13 (dddd, ^2J = 14.3, ^3J = 8.8, ^4J = 4.8, ^4J = 1.6, 1 H), 1.22 (s, 9 H), 0.32 (s, 9 H). ^{13}C NMR: 171.7, 152.6, 136.0, 116.1, 114.0, 82.6, 76.2, 52.1, 35.4, 28.3, 1.8. IR (film): 1700, 1245, 1190, 1090. Anal. Calcd: C, 43.91; H, 6.63. Found: C, 43.95; H, 6.67. CIMS: m/z 428 (M + NH_4^+, 100), 411 (M + H^+, 11).

(*Z*)-5-*tert*-Butoxy-4-[iodo(trimethylsilyl)methylidene]-1,7-octadiene (33). ^{1}H NMR: 5.90–5.78 (m, 1 H), 5.77–5.65 (m, 1 H), 5.10–4.95 (m, 4 H), 4.55 (dd, ^3J = 9.4, ^3J = 4.0, 1 H), 3.38 (ddt, ^2J = 13.4, ^3J = 7.2, ^4J =1.1, 1 H), 3.10 (ddt, ^2J = 13.4, ^3J = 4.4, ^3J = 2.2, 1 H), 2.12–2.08 (m, 2 H), 1.15 (s, 9 H), 0.30 (s, 9 H). ^{13}C NMR: 158.4, 137.7, 135.9, 116.6, 116.2, 83.6, 74.6, 39.9, 35.5, 28.5, 1.9. Structure confirmed by ^{1}H NMR CH COSY. IR (film): 1632, 1245, 1188, 1060. CIMS: m/z 410 (M + NH_4^+, 16), 393 (M + H^+, 23), 319 (M + H^+ - t-BuOH, 100).

Coupling Reactions Catalyzed by Palladium(0). General Procedure. After reaction with the first electrophile and then warming to rt, a mixture of the second electrophile E_2 (7 mmol) and $Pd(PPh_3)_4$ (0.245 mmol) in *N*,*N*-dimethylacetamide (10 mL) was added, followed by the addition of CuBr (7 mmol). The reaction was exothermic (+3 to +5 °C) and rapidly turned dark. After 1.0 to 4.0 h, the mixture was hydrolyzed and worked up as described for compounds of Table I. Products were purified by flash chromatography and eluted with cyclohexane:ethyl acetate 95:5 to 80:20. Yields are given in Table III.

(*E*,*E*,*E*)-6-(2-Propenyl)-5-*tert*-butoxy-7-(trimethylsilyl)-2,6,8-undecatrien-4-one (34). ^{1}H NMR: 6.83 (dt, ^3J = 15.0, ^3J = 6.9, 1 H), 6.74 (dt, ^3J = 15.0, ^4J = 1.6, 1 H), 6.02 (d, ^3J = 15.7, 1 H), 5.70–5.59 (m, 1 H), 5.56 (dt, ^3J = 15.7, ^3J = 6.7, 1 H), 5.10 (s, 1 H), 4.99 (dd, ^3J = 17.3, ^2J = 1.2, 1 H), 4.88 (dd, ^3J = 9.2, ^2J = 1.2, 1 H), 3.20–3.12 (m, 1 H), 2.93–2.87 (m, 1 H), 2.13 (dq, ^3J = 7.4, ^3J = 0.6, 2 H), 1.88 (br d, ^3J = 6.7, 3 H), 1.17 (s, 9 H), 1.03 (t, ^3J = 7.4, 3 H), 0.15 (s, 9 H). ^{13}C NMR: 201.0, 146.7, 142.2, 140.1, 137.8, 134.0, 130.3, 127.5, 116.1, 78.0, 75.3, 36.0, 28.4, 26.3, 18.4, 14.3, 0.8. Structure confirmed by CH COSY NMR. IR (film): 1688, 1623, 1245, 1070. CIMS: m/z 366 (M + NH_4^+, 8), 349 (M + H^+, 87), 275 (M + H^+ - t-BuOH, 100).

(*Z*,*E*,*E*)-*tert*-Butyl 6-*tert*-Butoxy-4-(trimethylsilyl)-5-(2-propenyl)-7-oxo-2,4,8-decatrienoate (35). ^{1}H NMR: 7.00 (br d, ^2J = 10.4, 1 H), 6.80 (d, ^3J = 17.0, 1 H), 6.78 (dq, ^3J = 17.0, ^3J = 7.0, 1 H), 5.65 (d, ^3J = 10.4) and 5.74–5.32 (m), 2 H all together, 5.17 (br d, ^3J = 17.0, 1 H), 4.78 (br d, ^2J = 10.0, 1 H), 4.65 (s, 1 H), 3.15 (br d, ^2J = 15.0, 1 H), 2.85 (br d, ^2J = 15.0, 1 H), 1.84–1.74 (m, 3 H), 1.35 (s, 9 H), 1.10 (s, 9 H), 0.12 (s, 9 H). ^{13}C NMR: 201.0, 165.0, 150.4, 144.4, 142.5, 136.9, 127.2, 119.2, 117.2, 79.5, 79.2 75.6, 36.8, 28.4, 28.3, 18.5, 1.4. Structure confirmed by CH COSY NMR. IR (film): 1710, 1622, 1688, 1145. CIMS: m/z 438 (M + NH_4^+, 100), 421 (M + H^+, 96).

(*E*,*E*)-1-(4-Methoxyphenyl)-1-(trimethylsilyl)-2-(2-propenyl)-3-*tert*-butoxy-1,5-heptadien-4-one (36). ^{1}H NMR: 7.13–7.11 and 6.79–6.71 (m, 4 H), 6.72 (dq partially hindered by aromatic protons, ^3J = 15.4, ^3J = 6.6, 1 H), 6.60 (dq, ^3J = 15.4, ^4J = 1.4, 1 H), 5.71–5.61 (m, 1 H), 4.99 (br dd, ^3J = 17.0, ^2J = 1.1, 1 H), 4.43 (s, 3 H), 3.21 (ddd, ^2J = 14.8, ^3J = 7.7, ^4J = 1.1, 1 H), 2.97 (ddd, ^2J = 14.8, ^3J = 5.5, ^4J = 1.4, 1 H), 1.80 (dd, ^3J = 6.6, ^4J = 1.4, 3 H), 1.02 (s, 9 H), 0.02 (s, 9 H). ^{13}C NMR: 200.7, 157.6, 148.3, 143.1, 142.2, 137.9, 136.0, 130.8, 128.1, 127.5, 116.2, 113.3, 113.0, 78.3, 75.5, 55.2, 36.3, 28.4, 18.4, 0.8. Structure confirmed by CH COSY NMR. IR (film): 1705, 1630, 1610, 1515, 1245, 1090. CIMS: m/z 418 (M + NH_4^+, 100), 401 (M + H^+, 89).

(*E*,*E*)-2-*tert*-Butoxy-4-(trimethylsilyl)-3-(2-propenyl)-1-phenyl-3,5-octadien-1-one (37). ^{1}H NMR: 7.91–7.86 (m, 2 H), 7.51–7.32 (m, 3 H), 5.92 (br d, ^3J = 16.5, 1 H), 5.78 (s, 1 H), 5.76–5.64 (m, 1 H), 5.36 (dt, ^3J = 15.9, ^3J = 6.3, 1 H), 4.91–4.79 (m, 2 H), 3.18–3.09 (m, 1 H), 3.03–2.95 (m, 1 H), 2.14 (ddt, ^3J = 7.7, ^3J = 6.3, ^4J = 2.7, 2 H), 1.16 (s, 9 H), 1.06 (t, ^3J = 7.7, 3 H), 0.1 (s, 9 H). ^{13}C NMR: 201.7, 145.0, 141.6, 138.2, 137.7, 133.8, 132.2, 130.4, 129.1, 128.0, 115.5, 76.6, 75.5, 34.8, 28.6, 26.3, 14.0, 0.5. Structure confirmed with CH COSY NMR. IR (film): 1718, 1690, 1592, 1245, 1080. CIMS: m/z 385 (M + H^+, 94), 311 (M + H^+ - t-BuOH, 100).

Cleavage of the *tert*-Butoxy Group. General Procedure. Anhydrous $FeCl_3$ (25 mg) was added to a solution of compound 11 (or 18) (1 mmol) in acetic anhydride (5 mL). The dark mixture was stirred at rt for 1 h (or 24 h for 18) until no starting material was left (follow by TLC). A saturated aqueous solution of Na_2HPO_4 (2.5 mL) was added and the mixture was stirred for 2 h. The aqueous layer was extracted twice with ether and the organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (cyclohexane:ethyl acetate 4:1) to give **38** (71%) or **39** (79%).

(*E*,*E*)-5-Acetoxy-4-[(trimethylsilyl)methylidene]-1,7-nonadien-6-one (38). ^{1}H NMR: 6.95 (dq, ^3J = 15.4, ^3J = 7.2, 1 H), 6.23 (dq, ^3J = 15.4, ^4J = 1.1, 1 H), 5.78–5.65 (m, 1 H), 5.75 (s, 1 H), 5.52 (s, 1 H), 5.11–5.03 (m, 2 H), 2.94 (br d, ^3J = 6.6, 2 H), 2.11 (s, 3 H), 1.86 (br d, ^3J = 8.3, 3 H). ^{13}C NMR: 193.2, 170.1, 147.2, 144.7, 135.4, 133.5, 127.0, 117.3, 81.0, 37.7, 20.9, 18.5. IR (film): 1742, 1702, 1630, 1245, 1225. CIMS: m/z 298 (M + NH_4^+, 27), 281 (M + H^+, 59), 221 (M + H^+ - AcOH, 100).

(*E*)-*N*-Phenyl-2-acetoxy-3-[(trimethylsilyl)methylidene]-5-hexenamide (39). ^{1}H NMR: 7.68 (br s, 1 H), 7.52–5.08 (m, 5 H), 5.87 (s, 1 H), 5.84–5.74 (m, 1 H), 5.62 (s, 1 H), 5.18–5.05 (m, 2 H), 3.15–3.01 (m, 2 H), 2.20 (s, 3 H), 0.18 (s 9 H). ^{13}C NMR: 169.1, 166.0, 148.4, 137.1, 135.6, 131.3, 129.0, 124.7, 120.0, 116.8, 77.7, 37.3, 21.1, 0.0. IR (*Nujol*): 3308, 1745, 1668, 1598, 1370. Mp = 82–4 °C. CIMS: m/z = 349 (M + NH_4^+, 64), 332 (M + H^+, 100).

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for all compounds described in the Experimental Section (57 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.