New Methodology for Conjugate Additions of Allylic Ligands to α,β-Unsaturated Ketones: Synthetic and Spectroscopic Studies

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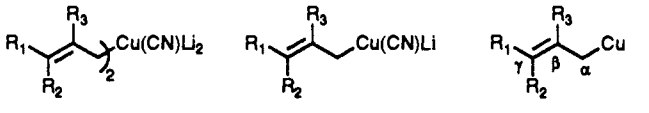
Abstract: Michael additions of allylic ligands, including allyl, methallyl, crotyl, and prenyl systems, to a variety of α,β-unsaturated ketones can be effected in synthetically useful yields with allylcopper reagents in the presence of trimethylchlorosilane. Low-temperature ^{13}C NMR spectral studies suggest that the allylic ligands are σ-bound to copper.

The paucity of copper(I)-initiated Michael addition reactions that efficiently transfer allylic ligands,[2] in particular to α,β-unsaturated ketones, seems odd given the generally accepted importance of organocopper reagents[3] and the inherent value of allylic organometallics.[4] The lack of usage of stoichiometric allylic cuprates stems, at least in part, from the continuous stream of (deservedly) "bad press" regarding even the simplest member of this clan of reagents (i.e., (diallylcopper)lithium).[5,6] From our spectroscopic measurements on both lower order (LO) and higher order (HO) cuprates has come an appreciation for their σ-bound status;[7] observations suggest that, if anything, they are overly reactive and in need of attenuation if discrimination between the 1,4- and 1,2-modes of addition is to be achieved. We now report a solution to this problem which provides, for the first time, a general method for the conjugate addition of allylic copper reagents to enones in synthetically useful yields.

Results and Discussion

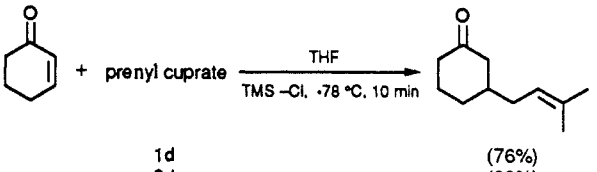
Initial attempts to deliver a simple allyl ligand to cyclohexenone by using either $(allyl)_2Cu(CN)Li_2$ (**1**) or (allyl)Cu(CN)Li (**2**) were completely unsuccessful. The products of 1,2-addition predominated, including those reactions where additives, e.g., $BF_3{\cdot}Et_2O$[8] and TMS-Cl,[9] were used as well. Only in the case



1 (HO allylic cuprate) **2** (LO allylic cuprate) **3** (allylcopper reagent)

a, $R_1 = R_2 = R_3 = H$ (allyl); **b**, $R_1 = R_2 = H$, $R_3 = CH_3$ (menthallyl); **c**, R_1 or $R_2 = CH_3$, $R_3 = H$ (crotyl); **d**, $R_1 = R_2 = CH_3$, $R_3 = H$ (prenyl)

of reagents containing a prenyl group (i.e., **1d** and **2d**) did selective reactions occur (eq 1), as we found this particular ligand to be, in general, the least reactive of the four studied.



(1)

1d	(76%)
2d	(89%)

Unexpectedly, even allylcopper gave a tertiary alcohol as the major side product (~25%) along with the desired ketone. The fact that allylcopper alone reacts at −78 °C was rather surprising since neutral, non-*ate* complexes "RCu" tend to be quite sluggish toward most of the standard organic substrates with which cuprates couple.[2] The atypical behavior of allylcopper (prepared from allyltributylstannane, MeLi, and LiCl-solubilized CuI in THF) encouraged us to examine it and its congeners spectroscopically. We applied the same ^{13}C NMR techniques used previously in our study of allyl ligand-containing Gilman and HO cyanocuprates, which provided strong evidence for the σ-bound status of these salts.[7]

The ^{13}C NMR spectrum of allylcopper in THF at −95 °C was rather startling: aside from weak peaks due to minor decomposition, there were no signals observable for this reagent! Although peak broadening due to α to γ exchange was likely, as seen with $(allyl)_2Cu(CN)Li_2$,[7] the loss of the β-carbon signal at these low temperatures suggests an even more rapid exchange than observed for allyl cuprates. Crotylcopper was more amenable to observation by ^{13}C NMR, the spectrum (taken at −95 °C) displaying significant peaks at δ 139.2 (C-β) and 101.7 (C-γ). Likewise,

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(1) (a) A. P. Sloan Fellow, 1984-1988; Camille and Henry Dreyfus Teacher-Scholar, 1984-1989. (b) Proctor & Gamble Predoctoral Fellow, 1989-1990.

(2) Lipshutz, B. H.; Sengupta, S. *Org. React.*, in press. Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagent*; Wiley: New York, 1980. Posner, G. H. *Org. React.* **1972**, *19*, 1.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 682.

(4) For a recent review, see: Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.

(5) See, for example: Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909. Hutchinson, D. K.; Fuchs, P. L. *Ibid.* **1986**, *27*, 1429. Bourgain-Commercon, M.; Foulon, J. P.; Normant, J. F. *J. Organomet. Chem.* **1982**, *228*, 321. Chuit, C.; Foulon, J. P.; Normant, J. F. *Tetrahedron* **1981**, *37*, 1385. Drouin, J.; Leyendecker, F.; Conia, J. M. *Ibid.* **1980**, *36*, 1203. Bertz, S. H.; Dabbagh, G. *Ibid.* **1989**, *45*, 425. Whitesides, G. M.; Fisher, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. House, H. O.; Fisher, W. F. *J. Org. Chem.* **1969**, *34*, 3615. House, H. O.; Wilkins, J. M. *Ibid.* **1978**, *43*, 2443. Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *Ibid.* **1986**, *51*, 1745.

(6) For some successful 1,4-additions of allylic cuprates, see: (a) Miginiac, Ph.; Daviaud, G.; Gerard, F. *Tetrahedron Lett.* **1979**, 1811. (b) Daviaud, G.; Maginiac, Ph. *Ibid.* **1972**, 997. (c) Corriu, R. J. P.; Guerin, C. M.; Boula, J. *Ibid.* **1981**, *22*, 2985. (d) Corey, E. J.; Boaz, N. W. *Ibid.* **1985**, *26*, 6019. (e) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4755. (f) *Ibid.* **1987**, *109*, 6137. (g) Enda, J.; Kuwajima, I. *Ibid.* **1985**, *107*, 5495. (h) Barbot, F.; Kadib-Elban, A.; Miginiac, Ph. *J. Organomet. Chem.* **1983**, *255*, 1.

(7) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J. *J. Org. Chem.* **1989**, *54*, 4977.

(8) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 4834; **1989**, *111*, 1351.

(9) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015. (b) Alexakis, A.; Berlan, J.; Besace, Y. *Ibid.* **1986**, *27*, 1047. (c) Sakata, H.; Kuwajima, I. *Ibid.* **1987**, *28*, 5719. (d) Nakamura, E.; Matsuzawa, S.; Horiguchi, Y.; Kuwajima, I. *Ibid.* **1986**, *27*, 4025, 4029. (e) Linderman, R. J.; Godfrey, A. *Ibid.* **1986**, *27*, 4553. (f) Johnson, C. R.; Marren, T. J. *Ibid.* **1987**, *28*, 27. (g) Chuit, C.; Foulon, J. P.; Normant, J. F. *Tetrahedron* **1980**, *36*, 2305. (h) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Ibid.* **1989**, *45*, 349. See also: Bergdahl, M.; Lindstedt, E.-V.; Nilsson, M.; Olsson, T. *Tetrahedron* **1989**, *45*, 535.

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prenylcopper gives peaks at δ 133.6 (C-β), 107.9 (C-γ), while methallylcopper shows C-β at δ 141.9 and C-γ at 110.5. Unfortunately, assignments for the upfield methyl group(s) on the olefinic portions of these allylic ligands, as well as the methylene carbons attached to copper, could not be made due to overlap with solvent and Bu_3SnMe peaks. Nonetheless, the chemical shifts described above, which are quite similar to those of the corresponding HO cyanocuprates,[7] are clearly indicative of σ-bound species.

Michael Additions of Allylic Copper Reagents

Considering the oftentimes remarkable benefits observed in organocopper chemistry attributable to the presence of Me_3SiCl,[9] we examined the combination of an allylic copper (i.e., **3**) together with 1 equiv of this additive in THF at −78 °C. Although it had been shown that TMS-Cl completely alters the composition of HO cyanocuprates (and hence would presumably impact on **1**),[10] there was no corresponding observable change in the ^{13}C NMR of **3b**. It was gratifying to find, therefore, that good to excellent yields of 1,4-allyl ligand transfer can indeed be realized utilizing this mixture of reagents. Table I summarizes our data, from which several noteworthy points emerge. Firstly, for cases involving transfer of a simple allyl ligand (entries 1–3), no extensive purification is needed for CuI.[9a] Moreover, in many situations, allylmagnesium bromide may be substituted for allyllithium, facilitating the procedure still further. Methallylcopper behaves much like its desmethyl analogue, although its ^{13}C NMR spectrum shows dissimilarities (vide supra). Both unhindered (entry 4) and α-substituted enones (entry 5) do not present obstacles toward 1,4-delivery. As the steric bulk is increased about the reactive site, however, products of 1,2-addition and reduction are competitive in the cyclohexenone series (entries 6, 7). With the corresponding γ,γ-disubstituted cyclopentenone (entry 8), no such problem arises.

The highly reactive nature of the allylic systems studied here, with the exception of the prenylcopper reagent, led to some unusual observations with selected substrates relative to what might be anticipated from prior art. For example, highly conjugated enones are typically more prone to cuprate additions than those enones lacking extended chromophores based on House's model using reduction potentials (E_{red}) as a guide.[11] With these reagents, however, precisely the opposite appears to prevail. Thus, 1,4-addition is favored with unsaturated ketones (e.g., entry 10) which do not bear more anodic E_{red} (as in entry 9). Interestingly, although only conjugate addition (and essentially no 1,2-addition) takes place, acid–base chemistry competes when methyl ketones are involved, thereby returning starting enone following hydrolysis of educt TMS enol ether. That these neutral, presumably polymeric organocopper reagents[12] are sufficiently basic to abstract protons at −78 °C is quite rare and serves as testimony to their atypical status. Such a pathway is not operative with the less basic prenyl species (entry 11), and vinylogous methyl ketones (e.g., entry 18) are not susceptible to this minor limitation.

The regiochemical issues surrounding use of prenyl- and crotylcopper reagents also deserve comment. Unlike Lewis acid based methodology of the precursor stannanes which react in an S_E2' sense,[13] these copper species couple predominantly, if not exclusively, at the α-position (entries 11–18). The crotylcopper derivative affords a ca. 3:1 mix of olefinic isomers favoring the *E* form, which is similar to the preference of crotyllithium to exist as a 3:2 mix of *E*:*Z* isomers.[14]

Finally, the simplicity of this process should be highlighted relative to other procedures involving copper reagents which rely on the presence of Me_3SiCl (or other additives[15]) for success.[9] While initial products of these couplings, as expected, are the corresponding TMS enol ethers, they are generated without recourse to HMPA,[9a,d] or amines,[9d,f] which are often considered essential for their formation. No special precautions are required for these reactions, although it is important to handle the LiCl-solubilized CuI/allyllithium mixture at −78 °C so as to prevent Wurtz-like degradation (see the Experimental Section).

Summary and Conclusions

From ^{13}C NMR spectral studies on several allylic copper species at very low temperatures has come an appreciation for their σ-bound status. These physical organic data have provided insight leading to the development of allylic copper reagents which possess the proper reactivity profiles, when combined with Me_3SiCl, to efficiently deliver in a 1,4-manner various allylic ligands to α,β-unsaturated ketones.

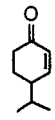
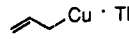
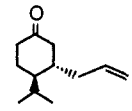
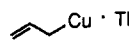
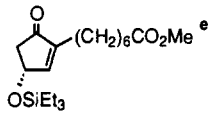
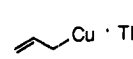
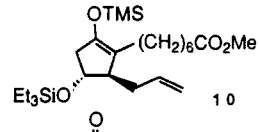
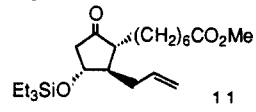
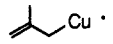
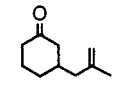
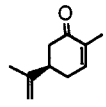
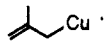
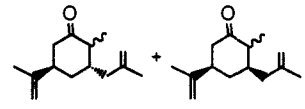
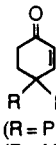
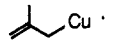
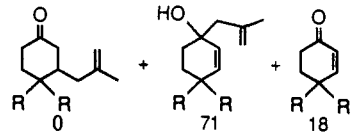
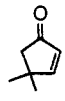
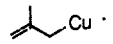
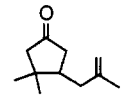
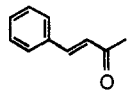
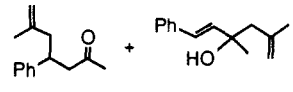
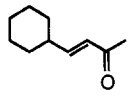
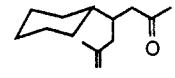
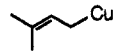
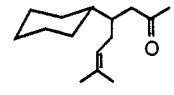
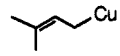
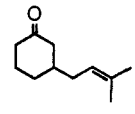
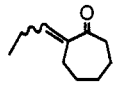
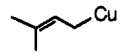
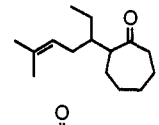
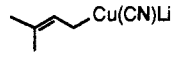
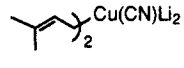
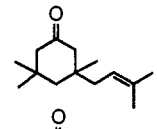
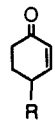
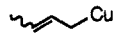
Experimental Section

THF and ether were distilled from sodium benzophenone ketyl under an atmosphere of dry N_2 immediately prior to use. CuI was purchased from Fischer Scientific Corp. and purified by the method of Whitesides under a nitrogen atmosphere.[17] Methyllithium, *n*-butyllithium, and allylmagnesium bromide were purchased from the Aldrich Chemical Co. and titrated by the method of Watson and Eastham.[18] Allyl-, methallyl-, crotyl-, and prenyltributylstannanes were prepared by the procedure of Keck with the corresponding bromide or chloride.[19] Methyl 5-oxo-3-[(triethylsilyl)oxy]-1-cyclopentene-1-heptanoate was generously supplied by G. D. Searle. 4,4-Dimethyl-2-cyclopentenone was prepared by the method of Holder.[20] 4,4-Diphenyl-2-cyclohexenone was prepared by a modification of the procedure of Zimmerman and Schuster.[21] The following compounds were purchased from the sources indicated and purified by standard techniques:[22] chlorotrimethylsilane, copper(I) cyanide, 4-isopropyl-2-cyclohexenone, 4-phenyl-3-buten-2-one, isophorone, allyl chloride (Aldrich); 3-methyl-2-butenyl bromide (Fluka); thiophene (Lancaster); (*E*)-2-butenyl bromide, 2-methyl-2-propenyl chloride (Pfaltz and Bauer). NMR spectra were obtained on Nicolet NT-300 or General Electric GN-500 spectrometers at 300 and 500 MHz, respectively. ^{13}C NMR observations of organometallic species were accomplished by techniques developed in these laboratories.[8] IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Mass spectra were obtained on an analytical VG 70-250 instrument. VPC analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 60-m fused silica J&W DB-5 capillary column. Flame-ionization detection was employed with H_2 as the carrier gas. Melting points were obtained on a Fischer-Johns hot-stage apparatus and are uncorrected.

Preparation of $(Allyl)_2Cu(CN)Li_2$. CuCN (0.0672 g, 0.75 mmol) was placed in a dry 10-mL round-bottom flask and the flask sealed with a septum. The flask was then evacuated with a vacuum pump and purged with argon. This process was repeated three times. THF (2 mL) was injected, and the slurry was cooled to −78 °C where MeLi (0.92 mL, 1.5 mmol) was added dropwise. The mixture was warmed to yield a colorless homogeneous solution which was recooled to −78 °C. Allyltributylstannane (0.47 mL, 1.4 mmol) was then injected via syringe, and the mixture was allowed to warm to room temperature for a period of 30 min to yield a bright yellow solution which was recooled to −78 °C. An aliquot (0.45 mL, 0.099 mmol) was then transferred via syringe under argon to a dry NMR tube (−78 °C) with the NMR tube spinner already in place. Prior to the addition of cuprate the NMR tube was fitted with a Teflon plug and a capillary insert (d_4-MeOH), purged thoroughly with

(10) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J.; Shirazi, A. *Tetrahedron Lett.* **1988**, *29*, 6677.
(11) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.
(12) Posner, G. H. *Org. React.* **1975**, *22*, 253.
(13) For an excellent overview of organotin chemistry, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. In *Tin in Organic Synthesis*; Butterworth: London, 1987.
(14) Seyferth, D.; Jula, T. F. *J. Organomet. Chem.* **1974**, *66*, 195.
(15) Use of $BF_3{\cdot}Et_2O$ with RCu (i.e., Yamamoto's reagent[16]) or RCu with both $BF_3{\cdot}Et_2O$ and TMS-Cl did not improve the chemoselectivity of addition. Moreover, with the prenylcopper–prenylcuprates plus $BF_3{\cdot}Et_2O$, the α-selectivity was also severely compromised.
(16) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* **1982**, *47*, 119.
(17) Linstrumelle, G.; Krieger, J. K.; Whitesides, G. M. *Org. Synth.* **1976**, *55*, 103.
(18) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.
(19) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797.
(20) Holder, R. W.; Daub, J. P.; Baker, W. E.; Gilbert, R. H., III; Graf, N. A. *J. Org. Chem.* **1982**, *47*, 1445.
(21) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.
(22) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1980.

Table I. Conjugate Addition Reactions of Allylic Copper Reagents in THF at −78 °C

Entry	Substrate	Organocopper/cuprate [a]	Time	Product(s) [b]	Yield(%) [c]
1			30 min		87
2		 [d] (+ MgBrI)			78
3	 **9**	 [d] (+ MgBrI)	15 min	 **10**  **11**	61 } 88 27 }
4			30 min		95
5			2 h	 [f]	87
					
6	(R = Ph)		30 min	0	71 18	89
7	(R = Me)		2 h	57	25 0	82 [g]
8			1 h		80
9			2 h		18 + 34 [h]
10			1 h		46 [i]
11			50 min		89
12			30 min		92
13			1 h	 [j]	61
14			30 min		77
15			20 min		56
			15 min		
16	(R = H)				89 [k]
17	(R = *i*-Pr)				93 [k,l]
18			30 min		73

[a] Most of these examples were done using 3 equiv of reagent; however, 1.5 equiv seems to be sufficient; see ref 17; 1 equiv of LiI is present in all cases except for entries 2 and 3. [b] All compounds gave satisfactory IR, NMR, MS, and HRMS data. [c] Isolated, following hydrolysis or fluoride removal of the silyl enol ether. [d] Reagent prepared from allyl Grignard, CuI, and Me_3SiCl. [e] Generously provided by G.D. Searle & Co. [f] Isolated as a 95:5 mixture of trans–cis isomers, epimeric at C-2 (60:40 and 53:47, respectively). [g] Run at −100 °C. [h] Most of the remaining mass is starting material. [i] 42% of the starting enone was recovered. [j] Isolated as a 1:1 mix of diastereomers. [k] A 3:1 mix of *E*:*Z* isomers. [l] A single diastereomer was formed.

argon for a minimum of 10 min, and then cooled to −78 °C, and the aliquot was transferred. The NMR tube was then fitted with a second Teflon plug to hold the capillary tube in place, and it was finally sealed with paraffin prior to the NMR experiment at −95 °C.

Preparation of (Prenyl)$_2$Cu(CN)Li$_2$. CuCN (0.0672 g, 0.75 mmol) and LiCl (0.0318 g, 0.75 mmol) were placed in a 10-mL round-bottom flask and sealed with a septum. The flask was then evacuated and purged with argon as described above. THF (1.5 mL) was injected, and the mixture stirred for 5 min to yield a yellow homogeneous solution which was cooled to −78 °C. Concurrently, a solution of prenyllithium (1.50 mmol) was prepared from prenyltri-*n*-butylstannane (0.52 mL, 1.50 mmol) and MeLi (0.89 mL, 1.50 mmol) in THF (1.6 mL) at −78 °C (15 min). This solution was then transferred via a dry ice cooled cannula to the CuCN/LiCl solution (−78 °C) to yield a bright yellow colored solution. An aliquot was then transferred to an NMR tube as described above.

Preparation of (Methallyl)$_2$Cu(CN)Li$_2$. Methallyllithium (2.04 mmol) was prepared from methallyltri-*n*-butylstannane (0.66 mL, 2.01 mmol) and MeLi (1.21 mL, 2.0 mmol) in THF (1.5 mL) as described above and added via a dry ice cooled cannula to a solution of CuCN (0.0916 g, 1.02 mmol)/LiCl (0.045 g, 1.05 mmol) in THF (0.7 mL) (−78 °C) to yield a bright yellow solution which was transferred to an NMR tube as described above.

Preparation of (Allyl)$_2$CuLi. A 10-mL round-bottom flask equipped with a stir bar was charged with CuI (0.1428 g, 0.75 mmol) and dry LiCl (0.0317 g, 0.75 mmol) and sealed with a septum. The flask was evacuated and purged with argon; this process was repeated three times. THF (1.0 mL) was injected, and the mixture stirred for 5 min to yield a yellow, homogeneous solution which was then cooled to −78 °C. Concurrently, a solution of allyllithium (1.50 mmol) was prepared from allyltri-*n*-butylstannane (0.47 mL, 1.50 mmol) and MeLi (0.94 mL, 1.50 mmol) in THF (1.0 mL) at −78 °C (15 min). Both solutions were then cooled to ca −100 °C, and the allyllithium was transferred to the CuI/LiCl solution via a dry ice cooled cannula to yield a tan solution. While the solution temperature was maintained at about −100 °C, an aliquot was transferred via a dry ice cooled cannula to a dry NMR tube as described above and cooled to ∼−100 °C. The NMR tube was then fitted with a second Teflon plug and sealed.

Preparation of (Allyl)$_3$Cu$_2$Li. Aggregate (allyl)$_3$Cu$_2$Li was prepared in the same manner as (allyl)$_2$CuLi. The following amounts of reagents were used: allyltri-*n*-butylstannane (0.47 mL, 1.5 mmol), MeLi (0.94 mL, 1.5 mmol), THF (1.5 mL), CuI (0.190 g, 1.0 mmol), and LiI (0.134 g, 1.00 mmol).

Preparation of Allyllithium. Allyltri-*n*-butylstannane (0.16 mL, 0.50 mmol) was added via syringe to a dry 10-mL round-bottom flask equipped with a stir bar and purged with argon. THF (4.0 mL) was injected, and the mixture was cooled to −78 °C where *n*-BuLi (0.19 mL, 0.50 mmol) was added via syringe. The mixture was stirred for 5 min to yield a bright yellow solution which was transferred via syringe to an NMR tube as described above.

4-Cyclohexyl-3-buten-2-one.[23] Prepared by the treatment of cyclohexanecarboxaldehyde with the anion of derved from dimethyl (2-oxopropyl)phosphonate. Purification was accomplished by flash chromatography (silica, petroleum ether/EtOAc, 19:1); TLC R_f 0.38 (silica, petroleum ether/EtOAc 19:1); IR (neat) 2920, 2855, 1741, 1672, 1625, 1449, 1358, 1351, 980 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (dd, 1 H, J_{am} = 16.1 Hz, J_{ax} = 6.8 Hz), 6.02 (dd, 1 H, J_{am} = 16.4 Hz, J_{ax} = 0.66 Hz), 2.25 (s, 3 H), 2.11–2.05 (m, 1 H), 1.80–1.56 (m, 4 H), 1.40–1.01 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 153.3, 128.7, 40.5, 31.7, 26.7, 25.8, 25.6.

1-Phenoxy-5-hepten-4-one. Prepared by the treatment of 3-phenoxypropyl bromide with magnesium turnings in THF to form the Grignard reagent followed by crotonaldehyde and subsequent oxidation of the resulting secondary alcohol with pyridinium chlorochromate. The product was purified by flash chromatography (silica, petroleum ether/EtOAc, 4:1); TLC R_f 0.45 (silica, petroleum ether/EtOAc, 3:1); IR (neat) 3065, 3043, 2942, 1738, 1670, 1633, 1600, 1589, 1494, 1473, 1442, 1377, 1290, 1245, 1174, 1136, 1080, 1046, 971, 753, 689, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.16 (m, 2 H), 7.03–6.71 (m, 4 H), 6.17–6.06 (m, 1 H), 3.98 (t, 2 H, J_{ax} = 6.06 Hz), 2.75 (t, 2 H, J_{ax} = 7.13 Hz), 2.14–2.03 (m, 2 H), 1.90–1.84 (m, 3 H).

Preparation of α-Propylidenecycloheptanone. To a solution containing 25 mmol of LDA in 15 mL of THF at −78 °C under a argon atmosphere was added cycloheptanone (2.95 mL, 25 mmol) via syringe, and the resulting solution was warmed to 0 °C for 5 min before being recooled to −78 °C where propionaldehyde (1.64 mL, 22.7 mmol) was added neat via syringe. The solution was then warmed to 0 °C for 1 h and quenched with a solution of 150 mL of MeOH and 40 mL of concentrated HCl. The reaction mixture was stirred for 3 h before extraction with 3 × 200 mL of Skelly solvent. The organic layers were combined, washed with saturated $NaHCO_3$ (150 mL), and dried over Na_2SO_4. The solvent was removed in vacuo, and the resulting residue was subjected to flash chromatography (Skellysolve/ether, 60:40) to yield 1.24 g (35%) of the enone as a colorless oil; TLC [Skellysolve/ether, 60:40] R_f 0.38; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.54 (t, 1 H, J = 7.5 Hz), 2.58–2.56 (m, 2 H), 2.41–2.38 (m, 2 H), 2.13 (q, 2 H, J = 7.5 Hz); IR (neat) 2930, 2860, 1690, 1620, 1450, 1325, 1180, 940 cm^{-1}; mass spectrum (EI), *m/z* (rel intensity) 152 (31), 123 (29), 95 (29), 82 (19), 81 (24), 73 (21), 67 (40), 55 (23), 43 (20); exact mass calculated for $C_{10}H_{16}O$ (M^+) 152.1201, found 152.1190.

Reaction of (Allyl)Cu·TMS-Cl·LiCl with 4-Isopropyl-2-cyclohexanone. CuI (0.400 g, 2.10 mmol) and dry LiCl (0.89 g, 2.10 mmol) were placed in a 10-mL round-bottom flask equipped with a stir bar and sealed with a septum. The flask was evacuated and purged with argon; the process was repeated three times. THF (1.5 mL) was injected, and the mixture was stirred for 5 min to yield a yellow, homogeneous solution which was then cooled to −78 °C. Concurrently, a solution of allyllithium (2.0 mmol) was prepared from allyltri-*n*-butylstannane (0.62 mL, 2.0 mmol) and MeLi (1.25 mL, 2.00 mmol) in THF (1.0 mL) at −78 °C (15 min). This solution was then transferred via a dry ice cooled cannula to the CuI/LiCl solution (−78 °C) to yield a tan solution. TMS-Cl (0.17 mL, 2.1 mmol) was added followed immediately by the neat addition of 4-isopropyl-2-cyclohexenone (0.11 mL, 0.75 mmol). The reaction was allowed to proceed for 30 min before being quenched with 5 mL of a saturated NH_4Cl solution. Extraction with 4 × 20 mL of ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was then removed in vacuo, and the resulting oil was treated with THF (5 mL) and TBAF (2.0 mL, 2.0 mmol) for 15 min. The solvent was again removed in vacuo, and the residue was subjected to flash chromatography (Skellysolve/ethyl acetate, 9:1) to yield 0.118 g (87%) of 3-(1-propen-3-yl)cyclohexanone as a colorless oil; TLC [Skellysolve/ethyl acetate, 9:1] R_f 0.28; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74–5.65 (m, 1 H), 5.05–5.00 (m, 2 H), 2.38–2.34 (m, 2 H), 2.26–1.80 (m, 4 H), 1.66–1.25 (m, 4 H), 0.97 (d, 3 H), 0.80 (d, 3 H); IR (neat) 3080, 2960, 1710, 1640, 1450, 990, 910 cm^{-1}; mass spectrum (EI), *m/z* (rel intensity) 180 (6), 139 (12), 111 (13), 97 (32), 95 (20), 83 (73), 69 (62), 55 (100), 43 (51); exact mass calculated for $C_{12}H_{20}O$ (M^+) 180.1513, found 180.1512.

Reaction of (Allyl)Cu·TMS-Cl·MgBrI with 4-Isopropyl-2-cyclohexenone. The organocopper reagent, (Allyl)Cu·TMS-Cl·MgBrI, was prepared as a tan slurry according to the above procedure. The following amounts of reagents were used: CuI (0.295 g, 1.55 mmol), LiBr (0.135 g, 1.55 mmol), THF (4 mL), allylmagnesium bromide (1.38 mL, 1.5 mmol), TMS-Cl (0.19 mL, 1.5 mmol), and 4-isopropyl-2-cyclohexenone (0.037 mL, 0.50 mmol). Reaction was allowed to proceed for 30 min at −78 °C. Quench, workup, and purification were as above to yield 0.090 g (78%) of 3-(1-propen-3-yl)cyclohexanone as a colorless oil.

Reaction of Methyl 5-Oxo-3-[(triethylsilyl)oxy]-1-cyclopentene-heptanoate (9). The organocopper reagent, (allyl)Cu·TMS-Cl·MgBrI, was prepared as a tan slurry according to the above procedure. The following amounts of reagents were used: CuI (0.238 g, 1.25 mmol), LiBr (0.1086 g, 1.25 mmol), THF (5 mL), allylmagnesium bromide (1.10 mL, 1.20 mmol), TMS-Cl (0.15 mL, 1.20 mmol), and **9** (0.1411 g, 0.400 mmol). Reaction was allowed to proceed for 15 min at −78 °C before being quenched with 5 mL of saturated NH_4Cl solution. Extraction with 4 × 30 mL of ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was removed in vacuo, and the resulting residue was subjected to flash chromatography (Skellysolve/ether, 95:5) to yield two products: methyl 5-oxo-3-[(triethylsilyl)oxy]-2-(1-propen-3-yl)-1-cyclopentaneheptanoate (**11**) (0.039 g, 27%) and methyl 1-[(trimethylsilyl)oxy]-4-[(triethylsilyl)oxy]-3-(1-propen-3-yl)-1-cyclopentene-2-heptanoate (**10**) (0.095 g, 61%), with a combined yield of 88% as yellow oils. **11**: TLC [Skellysolve/ether] R_f 0.28; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85–5.74 (m, 1 H), 5.08–5.00 (m, 2 H), 4.11–4.03 (q, 1 H, J = 6.0 Hz), 3.64 (s, 3 H), 2.57–2.52 (dd, 1 H), 2.33–2.12 (m, 5 H), 2.01–1.90 (m, 1 H), 1.87–1.80 (m, 1 H) 1.61–1.57 (m, 4 H), 1.31–1.23 (m, 4 H), 0.96–0.90 (m, 11 H), 0.57 (q, 6 H); ^{13}C NMR δ 217.8, 135.2, 117.4, 71.8, 52.4, 51.4, 48.9, 47.6, 35.4, 34.1, 29.4, 28.9, 26.6, 24.9, 6.8, 5.8, 4.8; IR (neat) 3080, 2940, 1740, 1640, 1440, 1240, 1170, 1110, 1010, 740 cm^{-1}; mass spectrum (EI), *m/z* (rel intensity) 368 (27), 367 (100), 233 (11), 213 (17), 171 (12), 129 (22), 122 (32), 103 (52), 87 (32), 79 (21), 75 (71), 67 (28), 59 (35); exact mass calculated for $C_{20}H_{35}O_4Si$ (M^+-Et) 367.2305, found 367.2318. **10**: TLC [Skellysolve/ether] R_f 0.55; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90–5.77 (m, 1 H), 5.07 (d, 1 H, J_{trans} = 17 Hz), 5.02 (d, 1 H, J_{cis} = 10 Hz), 4.11–4.10 (m, 1 H), 3.36 (s, 3 H), 2.67–2.58 (M, 2 H), 2.40–2.27 (m, 2 H), 2.09–2.03 (m, 2 H), 1.87–1.80 (m, 1 H), 1.52 (t, 2 H, J = 7 Hz),

(23) Oritani, T.; Matsunaga, T.; Yamashita, K. *Agric. Biol. Chem.* **1973**, *37*, 261.

1.45–1.10 (m, 8 H), 0.99 (t, 9 H, J = 7.5 Hz), 0.60 (q, 6 H, J = 7.5 Hz), 0.141 (s, 9 H); ^{13}C NMR δ 172.9, 144.1, 136.8, 117.3, 115.9, 73.4, 52.5, 50.8, 43.8, 36.2, 34.1, 29.5, 29.3, 27.6, 25.3, 24.5, 7.1, 5.3, 0.6; IR (neat) 3080, 2940, 2280, 1740, 1680, 1640, 1440, 1360, 1255, 1075, 1010, 845, 745 cm^{-1}; mass spectrum (EI), m/z (rel intensity) 468 (5), 429 (14), 428 (33), 427 (100), 115 (10), 87 (32), 75 (19), 73 (55), 59 (15); exact mass calculated for $C_{22}H_{43}O_4Si_2$ (M^+ – allyl) 427.2700, found 427.2734.

Reaction of Methallylcopper with 2-Cyclohexenone. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (1.04 g, 3.02 mmol), *n*-BuLi (0.93 mL, 3.01 mmol), THF (9.0 mL), CuI (0.623 g, 3.27 mmol), LiCl (0.148 g, 3.50 mmol), and TMS-Cl (0.652 g, 6.00 mmol). 2-Cyclohexenone (0.0963 g, 1.00 mmol) was added dropwise as a neat liquid and the mixture stirred at −78 °C for 30 min prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (3 mL) and treated at room temperature with TBAF (3.0 mL, 3.0 mmol) for 1 h. The solution was poured into H_2O (6 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a pale golden oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 7:1) yielding 3-(2-methylpropenyl)cyclohexanone (0.144 g, 0.946 mmol, 95%) as a colorless oil: TLC R_f 0.32 (silica, petroleum ether/EtOAc, 17:3); IR (neat) 3074, 2917, 1709, 1648, 1447, 1426, 1377, 1346, 1314, 1288, 1225, 1101, 1056, 889 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (s, 1 H), 4.68 (s, 1 H), 2.43–2.37 (m, 2 H), 2.34–2.23 (m, 1 H), 2.12–1.94 (m, 5 H), 1.93–1.86 (m, 1 H), 1.68 (s, 3 H), 1.68–1.60 (m, 1 H), 1.36–1.26 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 142.8, 112.3, 47.9, 45.2, 41.4, 36.7, 31.1, 25.1, 22.1; mass spectrum (CH_4 CIMS), m/z 153 (M + 1), 151, 149, 137, 133, 131, 123, 121, 113, 111, 109, 107, 105; exact mass calculated for $C_{10}H_{17}O$ 153.1225, found 153.1253.

Reaction of (2-Methallyl)copper with (*R*)-(−)-Carvone. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (0.522 g, 1.51 mmol), *n*-BuLi (0.625 mL, 1.50 mmol), THF (4.8 mL), CuI (0.314 g, 1.65 mmol), LiCl (0.071 g, 1.67 mmol), and TMS-Cl (0.342 g, 3.15 mmol). (*R*)-(−)-Carvone (0.057 g, 0.39 mmol) was added dropwise as a neat liquid and stirred at −78 °C for 2 h prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (8 mL), treated at 0 °C with a solution of H_2O/HOAc 8:1 (9 mL), and allowed to warm to room temperature over 4 h. The solution was quenched with saturated $NaHCO_3$ (16 mL) and extracted with ether (3 × 10 mL). The combined extracts were washed with H_2O then brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a pale golden oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 9:1) yielding 2-methyl-3-(2-methyl-2-propenyl)-5-(2-propenyl)cyclohexanone (0.068 g, 0.328 mmol, 87%) as a colorless oil which proved to be homogeneous to TLC. VPC analysis of the mixture showed four diastereomeric components [t_R (rel %)]: 12.51 min (36.7), 12.65 (59.0), 12.74 (1.8), 12.81 (2.5); TLC R_f 0.45 (silica, petroleum ether/EtOAc, 17:3); IR (neat) 3080, 2975, 2940, 1715, 1648, 1450, 1381, 1210, 892, 781, 779, 768 cm^{-1}; ^{1}H NMR (500 MHz $CDCl_3$) δ 4.84–4.61 (m, ca. 4 H), 2.77–1.39 (m, ca. 11 H), 1.38–0.83 (m, ca. 7 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.0, 213.1, 147.6, 147.1, 134.7, 112.6, 112.5, 111.0, 109.7, 49.7, 48.1, 46.2, 43.6, 42.6, 40.6, 40.3, 38.5, 37.9, 35.5, 32.8, 30.7, 22.0, 21.6, 21.4, 20.7, 14.5, 11.7; mass spectra (CH_4 EIGCMS) (in order of retention time) (isomer 1) m/z 99, 98, 86, 84, 79, 74, 70, 67, 58, 55, 49, 44; (isomer 2) 99, 98, 86, 84, 79, 74, 71, 70, 67, 64, 58, 55, 49, 44; (isomer 3) 99, 98, 93, 86, 84, 79, 74, 70, 67, 58, 55, 49, 44; (isomer 4) 99, 98, 86, 84, 79, 74, 70, 67, 58, 55, 49, 44; (CH_4 CIMS) (isomer 1) m/z 207 (M + 1), 191, 189, 179, 163, 151, 147, 135, 125, 123, 121, 119, 109, 107, 105, 97, 95, 93, 91, 83, 81, 79, 69, 67, exact mass calculated for $C_{14}H_{23}O$ 207.1751, found 207.1750; (isomer 2) 205 (M − 1), 191, 189, 179, 175, 163, 151, 147, 135, 125, 123, 121, 119, 109, 107, 105, 97, 95, 93, 91, 83, 81, 79, 71, 69, 67, exact mass calculated for $C_{14}H_{21}O$ 205.1614, found 205.1614; (isomer 4) 207 (M + 1), 191, 189, 179, 163, 151, 147, 135, 125, 123, 121, 119, 109, 107, 97, 95, 93, 91, 83, 81, 79, 71, 69, 67.

Reaction of Methallylcopper with 4,4-Diphenyl-2-cyclohexenone. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (0.724 g, 2.10 mmol), *n*-BuLi (0.84 mL, 2.06 mmol), THF (5.9 mL), CuI (0.391 g, 2.06 mmol), LiCl (0.112 g, 2.63 mmol), and TMS-Cl (0.428 g, 3.94 mmol). 4,4-Diphenyl-2-cyclohexenone (0.173 g, 0.698 mmol) was added dropwise as a solution in THF (1.1 mL) and stirred at −100 °C for 30 min prior to quenching. After removal of solvents in vacuo, the residue was taken up in MeOH (2 mL) and treated at 0 °C with K_2CO_3 (1 g) for 20 min. The solution was poured into H_2O (6 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 17:3) yielding 4,4-diphenylcyclohexanone (0.032 g, 0.127 mmol, 18%) as a white solid: mp 141–144.5 °C; TLC R_f 0.26 (silica, petroleum ether/EtOAc, 17:3), IR (KBr wafer) 3089, 3063, 2970, 2948, 2891, 1706, 1608, 1499, 1448, 1417, 1185, 770, 763, 713, 706 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 10 H), 2.68–2.64 (m, 4 H, ABX), 2.46–2.42 (m, 4 H, ABX); mass spectrum (HREIMS), m/z 250 (M^+), 222, 194, 193, 180, 179, 178, 165, 115, 91, 57; exact mass calculated for $C_{18}H_{18}O$ 250.1358, found 250.1376.

The remaining chromatography fractions which were shown to contain higher R_f material on TLC were recombined and evaporated in vacuo. The residue was taken up in THF (1.0 mL) and treated with TBAF (1.0 mL, 1.0 mmol) at room temperature over 3 h. The resulting pale orange solution was poured into ice/water (4 mL) and extracted with ether (3 × 5 mL). The organic extracts were combined, extracted with brine (10 mL), and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 17:3) yielding 1-(2-methyl-2-propenyl)-4,4-diphenyl-2-cyclohexen-1-ol (0.152 g, 0.498 mmol, 71%); TLC R_f 0.29 (silica, petroleum ether/EtOAc, 17:3); IR (neat) 3450, 3067, 3035, 2954, 1644, 1600, 1493, 1448, 1377, 1078, 994, 892, 788, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.18 (m, 10 H), 6.16 (d, 1 H, J = 10.3 Hz), 5.86 (d, 1 H, J = 10.1 Hz), 4.92 (s, 1 H), 4.76 (s, 1 H), 2.53–2.48 (m, 1 H), 2.34–2.25 (m, 1 H), 2.34–2.25 (m, 3 H), 1.87 (bs, 1 H, OH), 1.83 (s, 3 H), 1.72–1.68 (m, 2 H, ABX); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 147.3, 142.0, 136.1, 132.7, 128.15, 128.06, 127.8, 127.5, 125.9, 115.3, 115.1, 69.2, 49.5, 32.9, 32.8, 24.9, 14.1; mass spectrum (HREIMS), m/z 286 ($M^+ - H_2O$), 250, 249, 231, 182, 181, 178, 167, 165, 153, 152, 128, 121, 119, 117, 115, 91, 84, 82, 77, 55, 51, 47; exact mass calculated for $C_{22}H_{22}$ 286.1722, found 286.1709.

Reaction of Methallylcopper with 4,4-Dimethyl-2-cyclohexenone. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (0.820 g, 2.38 mmol), *n*-BuLi (0.90 mL, 2.26 mmol), THF (14.0 mL), CuI (0.552 g, 2.90 mmol), LiCl (0.152 g, 3.58 mmol), and TMS Cl (0.368 g, 3.39 mmol). 4,4-Dimethyl-2-cyclohexenone (0.094 g, 0.753 mmol) was added dropwise as a solution in THF (4.0 mL) and the mixture stirred at −100 °C for 2 h prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (4 mL) and treated at room temperature with TBAF (1.0 mL, 1.0 mmol) for 10 h. The solution was poured into H_2O (10 mL) and extracted with ether (3 × 10 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/acetone, 19:1) giving a mixture of 3-(2-methyl-2-propenyl)-4,4-dimethylcyclohexan-1-one and 1-(2-methyl-2-propenyl)-4,4-dimethyl-2-cyclohexen-1-ol (0.032 g, 0.127 mmol, 18%) as a colorless oil. Upon VPC analysis of the mixture, a 70:30 ratio of ketone to alcohol was observed. 3-(2-Methyl-2-propenyl)-4,4-dimethylcyclohexan-1-one was isolated as a white crystalline solid on repeated chromatography: mp 47–48.5 °C; TLC R_f 0.26 (silica, petroleum ether/acetone, 19:1); IR (KBr wafer) 3085, 2963, 2940, 2877, 1713, 1650, 1438, 1393, 1380, 1308, 1293, 1153, 889 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (s, 1 H), 4.66 (s, 1 H), 2.43–2.22 (m, 5 H), 2.03–1.96 (m, 1 H, ABM), 1.78–1.67 (m, 1 H, ABM), 1.78–1.67 (m, 3 H), 1.66 (s, 3 H), 1.06 (s, 3 H), 1.02 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.1, 143.0, 112.7, 44.0, 42.5, 40.5, 39.5, 38.3, 32.7, 28.7, 21.9, 19.4; mass spectrum (CH_4 HRCIGCMS), m/z 181 (M^+ + 1), 125, 109, 97, 83, 69, 55, 43; exact mass calculated for $C_{12}H_{21}O$ 181.1592, found 181.1574.

1-(2-Methyl-2-propenyl)-4,4-dimethyl-2-cyclohexen-1-ol was recovered as a colorless oil: TLC R_f 0.18 (silica, petroleum ether/acetone, 19:1); IR (neat) 3480, 2964, 2938, 1643, 1452, 1378, 1144, 1059, 889, 784 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (s, 2 H), 4.93 (s, 1 H), 4.78 (s, 1 H), 2.31–2.23 (m, 2 H), 1.84 (s, 3 H), 1.81–1.75 (m, 1 H), 1.70–1.57 (m, 4 H), 1.56 (bs, 1 H, OH), 1.50–1.44 (m, 1 H), 1.02 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 139.6, 130.2, 114.9, 69.5, 49.8, 33.7, 32.8, 31.9, 29.8, 28.0, 24.8; mass spectrum (CH_4 HRCIGCMS), m/z 163 ($M^+ - H_2O$), 162, 147, 125, 120, 119, 107, 106, 105, 96, 93, 91, 82, 81, 79, 77, 69, 67, 65, 55, 53, 51, 43; exact mass calculated for $C_{12}H_{19}$ 163.1486, found 163.1500.

Reaction of Methallylcopper with 4,4-Dimethyl-2-cyclopentenone. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (0.831 g, 2.41 mmol), *n*-BuLi (0.92 mL, 2.26 mmol), THF (7.0 mL), CuI (0.444 g, 2.33 mmol), LiCl (0.211 g, 2.43 mmol), and TMS-Cl (0.269 g, 2.47 mmol). 4,4-Dimethyl-2-cyclopentenone (0.083 g, 0.75 mmol) was added dropwise as a solution in THF (0.5 mL) and stirred at −78 °C for 20 min prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (2.25 mL) and treated at

room temperature with TBAF (2.25 mL, 2.25 mmol) for 30 min. The solution was poured into H_2O (5 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 9:1) yielding 3,3-dimethyl-4-(2-methyl-2-propenyl)cyclopentanone (0.100 g, 0.60 mmol, 80%) as a colorless oil: TLC R_f 0.44 (silica, petroleum ether/EtOAc, 17:3); IR (neat) 3081, 2960, 2938, 2899, 2878, 1738, 1647, 1453, 1405, 1388, 1362, 1276, 1184, 1140, 889 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.75 (s, 1 H), 4.70 (s, 1 H), 2.37 (dd, 1 H, J_{am} = 8.0 HZ, J_{ax} = 18.5 Hz), 2.28 (dd, 1 H, J_{am} = 14.0 Hz, J_{ax} = 3.0 Hz), 2.14 (s, 2 H), 2.13–2.08 (m, 1 H), 1.95 (dd, 1 H, J_{am} = 18.5 Hz, J_{ax} = 10.5 Hz), 1.87 (dd, 1 H, J_{am} = 14.0 Hz, J_{ax} = 3.0 Hz), 1.73 (s, 3 H), 1.18 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 218.3, 144.1, 111.5, 55.2, 43.9, 42.8, 38.5, 38.0, 27.5, 22.3, 21.7; mass spectrum (CH_4 HRCIMS), *m/z* 167 (M^+ + 1), 151, 149, 139, 125, 123, 111, 109, 97, 83, 82, 81, 67; exact mass calculated for $C_{11}H_{18}O$ 167.1399, found 167.1418.

Reaction of Methallylcopper with 4-Phenyl-3-buten-2-one. The organocopper was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (0.854 g, 2.47 mmol), *n*-BuLi (0.94 mL, 2.25 mmol), THF (6.5 mL), CuI (0.473 g, 2.48 mmol), LiCl (0.108 g, 2.55 mmol), and TMS-Cl (0.513 g, 4.73 mmol). 4-Phenyl-3-buten-2-one (0.113 g, 0.77 mmol) was added dropwise as a solution in THF (1.5 mL) and stirred at −78 °C for 30 min prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (2.3 mL) and treated at room temperature with TBAF (2.3 mL, 2.3 mmol) for 3 h. The solution was poured into H_2O (5 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 9:1) yielding two products along with starting enone. 6-Methyl-4-phenyl-6-hepten-2-one (0.27 g, 0.259 mmol, 34%): colorless oil; TLC R_f 0.45 (silica, petroleum ether/EtOAc, 17:3); IR (neat) 3079, 3039, 2978, 2942, 1715, 1650, 1606, 1497, 1456, 1361, 1160, 894, 790, 759, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2 H), 7.20–7.15 (m, 3 H), 4.71 (s, 1 H), 4.62 (s, 1 H), 3.40–3.35 (m, 1 H), 2.73–2.70 (m, 2 H), 2.31 (d, 2 H, *J* = 8.0 Hz), 2.00 (s, 3 H), 1.67 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 144.4, 143.3, 128.4, 127.3, 126.4, 112.8, 49.8, 45.1, 38.9, 30.7, 22.1; mass spectrum (HREIMS), *m/z* 202 (M^+), 145, 144, 129, 104, 103, 91, 77, 43; exact mass calculated for $C_{14}H_{18}O$ 202.1376, found 202.1367. 3,5-Dimethyl-1-phenyl-1,5-hexadien-3-ol (0.052 g, 0.136 mmol, 18%): colorless oil; TLC R_f 0.35 (silica, petroleum ether/EtOAc 17:3); IR (neat) 3450, 3064, 3033, 2975, 2932, 1640, 1492, 1448, 1373, 1091, 970, 894, 747, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2 H), 7.32–7.29 (m, 2 H), 7.23–7.20 (m, 1 H), 6.60 (d, 1 H, *J* = 16.0 Hz), 6.30 (d, 1 H, *J* = 16.0 Hz), 4.95 (s, 1 H), 4.81 (s, 1 H), 2.39 (s, 2 H), 2.03 (s, 1 H), 1.74 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 137.0, 136.9, 128.6, 127.3, 126.6, 126.4, 115.5, 50.9, 28.7, 24.8; mass spectrum (HREIMS), *m/z* 186 ($M^+ - H_2O$), 185, 147, 145, 129, 105, 91; exact mass calculated for $C_{14}H_{16}$ 185.1286, found 185.1308.

Reaction of (2-Methallyl)copper with 4-Cyclohexyl-3-buten-2-one. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: tri-*n*-butylmethallylstannane (0.852 g, 2.47 mmol), *n*-BuLi (0.90 mL, 2.26 mmol), THF (5.5 mL), CuI (0.444 g, 2.33 mmol), LiCl (0.106 g, 2.50 mmol), and TMS-Cl (0.428 g, 3.92 mmol). 4-Cyclohexyl-3-buten-2-one (0.114 g, 0.750 mmol) was added dropwise as a solution in THF (1.5 mL) and stirred at −78 °C for 1 h prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (2.3 mL) and treated at room temperature with TBAF (2.3 mL, 2.3 mmol) for 40 min. The solution was poured into H_2O (5 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 19:1) yielding the starting enone (0.048 g, 42%) and 4-cyclohexyl-6-methyl-6-hepten-2-one (0.071 g, 0.342 mmol, 46%) as a colorless oil: TLC R_f 0.16 (silica, petroleum ether/EtOAc, 19:1); IR (neat) 3083, 2922, 2859, 1719, 1650, 1452, 1379, 1361, 1162, 891 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 4.73 (s, 1 H), 4.65 (s, 1 H), 2.36 (dd, 1 H, J_{AM} = 6.0 Hz, J_{AX} = 17.0 Hz), 2.28 (dd, 1 H, J_{AM} = 6.0 Hz, J_{AX} = 17.0 Hz), 2.12 (s, 3 H), 2.11–2.05 (m, 2 H), 1.81 (dd, 1 H, J_{AM} = 4.0 Hz, J_{AX} = 15.0 Hz), 1.76–1.70 (m, 2 H), 1.69 (s, 3 H), 1.68–1.62 (m, 1 H), 1.61–1.53 (m, 2 H), 1.33–1.26 (m, 1 H), 1.24–1.15 (m, 2 H), 1.14–1.06 (m, 1 H), 1.03–0.93 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 209.1, 144.7, 112.1, 45.2, 40.6, 40.3, 36.4, 30.4, 29.9, 29.3, 26.7, 21.9; mass spectrum (HREIMS), *m/z* 208 (M^+), 150, 135, 125, 109, 108, 107, 95, 94, 93, 82, 81, 79, 71, 69, 68, 67, 55, 43; exact mass calculated for $C_{14}H_{24}O$ 208.1871, found 208.1849.

Reaction of Prenylcopper·TMS-Cl with 4-Cyclohexyl-3-buten-2-one. The organocopper reagent was prepared as a red solution as described above with the following quantities of reagents: tri-*n*-butylprenylstannane (0.85 g, 2.35 mmol), *n*-BuLi (0.90 mL, 2.26 mmol), THF (5.5 mL), CuI (0.453 g, 2.38 mmol), LiCl (0.120 g, 2.84 mmol), and TMS-Cl (0.428 g, 3.94 mmol). 4-Cyclohexyl-3-buten-2-one (0.118 g, 0.773 mmol) was added dropwise as a solution in THF (1.5 mL) and stirred at −78 °C for 50 min prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (2.3 mL) and treated at room temperature with TBAF (2.3 mL, 2.3 mmol) for 30 min. The solution was poured into H_2O (5 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a colorless oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 19:1) yielding 4-cyclohexyl-7-methyl-6-octen-2-one (0.151 g, 0.684 mmol, 89%) as a colorless oil: TLC R_f 0.32 (silica, petroleum ether/EtOAc, 19:1); IR (neat) 2915, 2850, 1710, 1447, 1358, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.08–5.01 (m, 1 H), 2.36 (dd, 1 H, J_{AM} = 5.6 Hz, J_{AX} = 16.3 Hz), 2.25 (dd, 1 H, J_{AM} = 6.6 Hz, J_{AX} = 16.3 Hz), 2.11 (s, 3 H), 2.15–1.96 (m, 1 H), 1.92–1.83 (m, 2 H), 1.77–1.70 (m, 2 H), 1.69–1.54 (m, 9 H), 1.34–1.05 (m, 4 H), 1.03–0.94 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 132.6, 123.2, 45.6, 40.5, 40.0, 30.2, 30.0, 29.7, 26.7, 25.8, 17.7; mass spectrum (HREIMS), *m/z* 223 (M^+ + 1), 221, 206, 203, 166, 165, 164, 163, 153, 149, 135, 129, 123, 121, 110, 109; exact mass calculated for $C_{15}H_{26}O$ 223.2101, found 223.2082.

Reaction of 2-Cyclohexenone with (Prenyl)Cu·TMS-Cl. The reagent (prenyl)Cu·TMS-Cl was prepared as a dark brown solution according to the above procedure. The following amounts of reagents were used: CuI (0.4495 g, 2.360 mmol), LiBr (0.205 g, 2.36 mmol), THF (3.0 mL), tri-*n*-butylprenylstannane (0.780 mL, 2.25 mmol), *n*-BuLi (0.900 mL, 2.25 mmol), THF (3.0 mL), TMS-Cl (0.286 mL, 2.25 mmol), and 2-cyclohexenone (0.073 mL, 0.75 mmol). Reaction was allowed to proceed for 30 min at −78 °C before being quenched with a saturated NH_4Cl solution (10.0 mL). Extraction with 5 × 30 mL ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was removed in vacuo, and the resulting oil was subjected to flash chromatography (Skellysolve/ethyl acetate, 9:1) to yield 0.111 g (92%) of 3-(2-methyl-2-buten-4-yl)cyclohexane as a colorless oil: TLC [hexane/ethyl acetate, 95:5] R_f 0.28; ^1H NMR, δ 5.08 (t, 1 H, *J* = 7.5 Hz), 2.40–2.30 (m, 2 H), 2.26–2.19 (m, 1 H), 2.04–1.95 (m, 3 H), 1.88–1.85 (m, 2 H), 1.81–1.75 (m, 1 H), 1.68 (s, 3 H), 1.66–1.58 (m, 1 H), 1.57 (s, 3 H), 1.37–1.28 (m, 1 H); IR (neat) 2900, 1710, 1450, 1225 cm^{-1}; mass spectrum (EI), *m/z* (rel intensity) 166 (9), 110 (11), 108 (15), 97 (29), 69 (53), 55 (19); exact mass calculated for $C_{11}H_{18}O$ (M^+) 166.1358, found 166.1355.

Reaction of α-Propylidenecycloheptan-1-one with (Prenyl)Cu·TMS-Cl. The reagent (prenyl)Cu·TMS-Cl was prepared as a dark brown solution according to the above procedure. The following amounts of reagents were used: CuI (0.3599 g, 1.890 mmol), LiBr (0.1641 g, 1.890 mmol), THF (2.0 mL), prenyltri-*n*-butylstannane (0.65 mL 1.8 mmol), *n*-BuLi (0.72 mL, 1.8 mmol), THF (3.0 mL), TMS-Cl (0.23 mL, 1.8 mmol), α-propylidenecycloheptan-1-one (0.092 g, 0.60 mmol), and THF (1.0 mL). Reaction was allowed to proceed for 60 min before being quenched with a saturated NH_4Cl solution (10.0 mL). Extraction with 4 × 30 mL ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was removed in vacuo, and the resulting oil was treated with THF (3.0 mL) and TBAF (3.0 mL, 3.0 mmol) for 20 min. The solvent was again removed in vacuo, and the residue was subjected to column chromatography (Skellysolve/ether, 95:5) to yield 0.82 g (62%) of 2-(2-methyl-2-hepten-5-yl)cycloheptan-1-one as a colorless oil: TLC [Skellysolve/ether, 95:5] R_f 0.31; ^1H NMR δ 5.04–5.00 (m, 1 H), 2.50 (tt, 1 H), 2.42–2.33 (m, 2 H), 2.02–1.72 (m, 8 H), 1.66 (s, 3 H), 1.55 (s, 3 H), 1.52–1.15 (m, 5 H), 0.83 (t, 3 H); IR (neat) 2920, 1680, 1450, 1375, cm^{-1}; mass spectrum (EI), *m/z* (rel intensity) 222 (1), 112 (6), 111 (10), 110 (100), 95 (34), 69 (16), 55 (13); exact mass calculated for $C_{15}H_{22}O$ (M^+) 222.1984, found 222.1994.

Reaction of α-Propylidenecycloheptan-1-one with (Prenyl)Cu(CN)Li·TMS-Cl. The cuprate (prenyl)Cu(CN)Li·TMS-Cl was prepared as a dark tan solution in the same manner as the organocopper reagents. The following amounts of reagents were used: CuCN (0.2257 g, 2.520 mmol), LiCl (0.107 g, 2.52 mmol), prenyltri-*n*-butylstannane (0.84 mL, 2.4 mmol), *n*-BuLi (0.96 mL, 2.4 mmol), THF (8 mL), TMS-Cl (0.30 mL, 2.4 mmol), and α-propylidenecycloheptanone (0.123 g, 0.800 mmol). Reaction was allowed to proceed 30 min before being quenched, worked up, and purified in the manner described just above to yield 0.136 g (77%) of 2-(2-methyl-2-hepten-5-yl)cycloheptan-1-one as a colorless oil.

Reaction of Isophorone with (Prenyl)$_2$Cu(CN)Li$_2$. CuCN (0.81 g, 0.90 mmol) was placed in a dry 10-mL round-bottom flask and sealed with a septum. The flask was evacuated with a vacuum pump and

purged with argon, and this process was repeated three times. THF (1.0 mL) was injected, and the resulting slurry was cooled to −78 °C where MeLi (1.121 mL, 1.80 mmol) was added dropwise via syringe. The mixture was allowed to warm to 0 °C to yield a colorless, homogeneous solution which was treated with prenyltri-*n*-butylstannane (0.63 mL, 1.8 mmol) and stirred for a period of 20 min. The resulting bright yellow solution was recooled to −78 °C and treated with TMS-Cl (1 equiv) followed immediately by the neat addition of isophorone (0.090 mL, 0.60 mmol). The reaction mixture was allowed to stir for 10 min at −78 °C before being quenched with 5 mL of saturated NH_4Cl. Extraction with 4 × 50 mL ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was removed in vacuo and the residue treated with TBAF (3.0 mL, 3.0 mmol) in THF (3.0 mL) for a period of 15 min. The solvent was again removed in vacuo and the residue subjected to flash chromatography (hexane/ethyl acetate, 95:5) to yield 0.070 g (56%) of (3,5,5-trimethyl-3-(2-methyl-2-buten-4-yl)cyclohexan-1-one as a colorless oil: TLC [Skellysolve/ethyl acetate, 95:5] R_f 0.36; ^{1}H NMR δ 5.14 (t, 1 H, J = 8.5 Hz), 2.22–2.04 (m, 4 H), 1.96 (d, 2 H, J = 7.5 Hz), 1.71 (s, 3 H), 1.63 (d, 1 H, J = 14 Hz), 1.57 (s, 3 H), 1.45 (d, 1 H, J = 7.5 Hz), 1.03 (s, 3 H), 1.01 (s, 3 H), 0.97 (s, 3 H); IR (neat) 2950, 1705, 1350, 1100, 855 cm^{-1}, mass spectrum (EI), m/z (rel intensity) 208 (3), 206 (8), 191 (27), 149 (77), 139 (36), 83 (81), 69 (98), 55 (100), 43 (41); exact mass calculated for $C_{14}H_{24}O$ (M^+) 208.1827, found 208.1820.

Reaction of 2-Cyclohexen-1-one with (Crotyl)Cu·TMS-Cl. The reagent (crotyl)Cu·TMS-Cl was prepared as a dark solution according to the procedure above. The following amounts of reagents were used: CuI (0.4495 g, 2.360 mmol), LiCl (0.100 g, 2.36 mmol), THF (3.0 mL), crotyltri-*n*-butylstannane (0.750 mL, 2.25 mmol), *n*-BuLi (0.900 mL, 2.25 mmol), TMS-Cl (0.286 mL, 2.25 mmol), and 2-cyclohexen-1-one (0.073 mL, 0.75 mmol). Reaction was allowed to proceed for 15 min before being quenched with a saturated NH_4Cl solution. Extraction with 5 × 30 mL of ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was removed in vacuo and the resulting residue subjected to flash chromatography (Skellysolve/ethyl acetate, 9:1) to yield (0.105 g, 92%) a 3:1 mixture of *trans*- and *cis*-3-(2-butenyl)cyclohexan-1-one as a colorless oil: TLC [hexane/ethyl acetate, 9:1] R_f 0.27; ^{1}H NMR ($CDCl_3$, mixture) δ 5.56–5.43 (m, vinyl H, cis), 5.45–5.30 (m, mixture cis and trans vinyl H), 2.45–2.18 (m, 4 H), 2.10–1.95 (m, 3 H), 1.90–1.75 (m, 2 H), 1.62–1.58 (m, 3 H), 1.38–1.23 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 211.87, 128.05 (trans), 127.26 (cis), 127.20 (trans), 125.67 (cis), 47.76 (cis), 47.69 (trans), 41.34, 39.48, 39.37, 39.20, 33.49, 30.84, 25.14, 17.82 (trans), 12.81 (cis); IR (neat) 2940, 1710, 1450, 1230, 970 cm^{-1}; GCMS (EI) for trans product m/z 152, 123, 110, 97, 78, 67, 55; HRMS (CI) exact mass calculated for $C_{10}H_{17}O$ (M^+ + 1) 153.1280, found 153.1285; GCMS (EI) for cis product m/z 152, 123, 110, 97, 78, 67, 55; HRMS (CI) exact mass calculated for $C_{10}H_{17}O$ (M^+ + 1) 153.1280, found 153.1299.

Reaction of 4-Isopropyl-2-cyclohexenone with (Crotyl)Cu·TMS-Cl. The reagent (crotyl)Cu·TMS-Cl was prepared as a dark solution according to the above procedure. The following amounts of reagents were used: CuI (0.3051 g, 1.60 mmol), LiCl (0.0678 g, 1.60 mmol), THF (3.0 mL), crotyltri-*n*-butylstannane (0.500 mL, 1.50 mmol), *n*-BuLi (0.60 mL, 1.5 mmol), TMS-Cl (0.19 mL, 1.5 mmol), and 4-isopropyl-2-cyclohexenone (0.073 mL, 0.50 mmol). Reaction was allowed to proceed for 20 min before being quenched with a saturated NH_4Cl solution (10 mL). Extraction with 5 × 30 mL of ether was followed by combining the organic layers and drying over Na_2SO_4. The solvent was removed in vacuo and the residue treated with THF (5 mL) and TBAF (3.0 mL, 3.0 mmol) and stirred for 15 min. The solvent was again removed in vacuo, and the resulting crude material was subjected to flash chromatography (hexanes/ethyl acetate, 95:5) to yield (0.097 g, 93%) a 3:1 mixture of *trans*- and *cis*-3-(2-butenyl)-4-isopropylcyclohexan-1-one as a colorless oil: TLC [hexane/ethyl acetate, 95:5] R_f 0.35; ^{1}H NMR ($CDCl_3$), δ 5.57–5.52 (m, vinyl H cis; minor product), 5.46–5.28 (m, mixture cis + trans vinyl H, cis was major product), 2.36–2.32 (m, 2 H), 2.37–2.21 (m, 2 H), 2.12–1.91 (m, 4 H), 1.82–1.75 (m, 1 H), 1.64 (d, 2 H), 1.51–1.34 (m, 2 H), 0.96 (d, 3 H), 0.79 (d, 3 H); IR (neat) 2950, 1710, 1450, 970 cm^{-1}; mass spectrum (EI), m/z (rel intensity) 194 (17), 139 (64), 136 (15), 121 (16), 97 (53), 95 (20), 83 (71), 81 (22), 79 (19), 69 (62), 67 (22), 55 (100), 43 (36); exact mass calculated for $C_{13}H_{22}O$ (M^+) 194.1671, found 194.1674.

Reaction of (Crotyl)Cu·TMS-Cl with 1-Phenoxy-5-hepten-4-one. The organocopper reagent was prepared as a deep red solution as described above with the following quantities of reagents: crotyltri-*n*-butylstannane (0.612 g, 1.78 mmol), *n*-BuLi (0.70 mL, 1.76 mmol), THF (5.0 mL), CuI (0.347 g, 1.82 mmol), LiCl (0.171 g, 4.03 mmol), and TMS-Cl (0.385 g, 3.55 mmol). 2-Cyclohexenone (0.120 g, 0.587 mmol) was added dropwise as a solution in THF (2.0 mL) and stirred at −78 °C for 30 min prior to quenching. After removal of the solvents in vacuo, the residue was taken up in THF (1.5 mL) and treated at room temperature with TBAF (1.5 mL, 1.5 mmol) for 1 h. The solution was poured into H_2O (5 mL) and extracted with ether (3 × 5 mL). The combined extracts were washed with brine and dried over Na_2SO_4. The solution was filtered and evaporated in vacuo to give a pale golden oil which was subjected to flash chromatography on silica gel (petroleum ether/EtOAc, 19:1) yielding 6-methyl-1-phenoxy-8-decen-4-one (0.112 g, 0.431 mmol, 73%) as an inseparable 3:1 mixture (VPC) of *E* and *Z* isomers in the form of a colorless oil: TLC R_f 0.60 (silica, petroleum ether/EtOAc, 17:3); IR (neat) 2965, 2938, 1712, 1601, 1589, 1497, 1246, 1038, 754, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2 H), 6.95–6.92 (m, 1 H), 6.89–6.85 (m, 2 H), 5.58–5.30 (m, 2 H), 3.96 (t, 2 H, J = 5.5 Hz), 2.62–2.58 (m, 2 H), 2.45–2.14 (m, 2 H), 2.08–2.00 (m, 5 H), 1.65–1.56 (m, 2 H), 1.35–1.08 (m, 1 H), 0.92–0.86 (m, 3 H; ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.4, 129.0, 126.9, 120.6, 116.4, 114.4, 66.7, 49.6, 39.9, 39.6, 39.5, 36.1, 33.8, 29.7, 23.3, 19.8, 17.9; mass spectrum (CH_4, HRCIGCMS) (isomer 1) m/z 261 (M^+ + 1), 169, 167, 163, 149, 123, 111, 95, 82, 71, 69, 55, 43, exact mass for $C_{17}H_{25}O_2$ 261.1854, found 261.1859; (isomer 2) m/z 261 (M^+ + 1), found 261.1819.

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Registry No. 9, 112713-92-5; **10**, 126377-61-5; **11**, 126377-62-6; $PhO(CH_2)_3COCH{=}CHCH_3$, 126377-58-0; $(allyl)_2Cu(CN)Li_2$, 91328-60-8; $(prenyl)_2CuLi_2$, 122700-73-6; $(methallyl)_2Cu(CN)Li_2$, 122700-72-5; $(allyl)_2CuLi$, 21500-57-2; $(allyl)_3Cu_2Li$, 126421-35-0; α-propylidenecycloheptan-1-one, 126377-59-1; 3-phenoxypropyl bromide, 588-63-6; croton aldehyde, 4170-30-3; cycloheptanone, 502-42-1; propionaldehyde, 123-38-6; 4-isopropyl-2-cyclohexenone, 500-02-7; 2-cyclohexanone, 930-68-7; (*R*)-(−)-carvone, 6485-40-1; 4,4-diphenyl-2-cyclohexenone, 4528-64-7; 4,4-dimethyl-2-cyclohexenone, 1073-13-8; 4,4-dimethyl-2-cyclopentenone, 22748-16-9; 4-phenyl-3-buten-2-one, 122-57-6; 4-cyclohexyl-3-buten-2-one, 7152-32-1; isophorone, 78-59-1; *trans*-3-allyl-4-isopropylcyclohexanone, 126377-60-4; 3-(2-oxopropyl)cyclohexanone, 937-45-1; 2-methyl-3-(2-methyl-2-propenyl)-5-(2-propenyl)-cyclohexanone (isomer 1), 126377-63-7; 2-methyl-3-(2-methyl-2-propenyl)-5-(2-propenyl)cyclohexanone (isomer 2), 126377-64-8; 2-methyl-3-(2-methyl-2-propenyl)-5-(2-propenyl)cyclohexanone (isomer 3), 126377-78-4; 2-methyl-3-(2-methyl-2-propenyl)-5-(2-propenyl)cyclohexanone (isomer 4), 126377-79-5; 3-(2-methyl-2-propenyl)-4,4-diphenyl-2-cyclohexen-1-one, 126377-65-9; 1-(2-methyl-2-propenyl)-4,4-diphenyl-2-cyclohexen-1-ol, 126421-34-9; 3-(2-methyl-2-propenyl)-4,4-dimethylcyclohexen-1-one, 126377-66-0; 1-(2-methyl-2-propenyl)-4,4-dimethyl-2-cyclohexen-1-ol, 126377-67-1; 3,3-dimethyl-4-(2-methyl-2-propenyl)cyclopentanone, 126377-68-2; 6-methyl-4-phenyl-6-hepten-2-one, 75359-62-5; 3,5-dimethyl-1-phenyl-1,5-hexadien-3-ol, 126377-69-3; 4-cyclohexyl-6-methyl-6-hepten-2-one, 126377-70-6; 4-cyclohexyl-7-methyl-6-octen-2-one, 126377-71-7; 3-(2-methyl-2-buten-4-yl)cyclohexane, 29843-83-2; (*R**,*R**)-2-(2-methyl-2-hepten-5-yl)cycloheptan-1-one, 126377-72-8; (*R**,*S**)-2-(2-methyl-2-hepten-5-yl)cycloheptan-1-one, 126377-73-9; 3,5,5-trimethyl-3-(2-methyl-2-buten-4-yl)cyclohexen-1-one, 126377-74-0; (*E*)-3-(2-buten-4-yl)cyclohexan-1-one, 126377-75-1; (*Z*)-3-(2-buten-4-yl)cyclohexan-1-one, 126457-07-6; (*E*)-3-(2-butenyl)-4-isopropylcyclohexan-1-one, 126377-76-2; (*Z*)-3-(2-butenyl)-4-isopropylcyclohexan-1-one, 126454-81-7; (*Z*)-6-methyl-1-phenoxy-8-decen-4-one, 126377-77-3; (*E*)-6-methyl-1-phenoxy-8-decen-4-one, 126377-80-8; 4,4-diphenylcyclohexanone, 4528-68-1.