Efficient Synthesis of 2-Mono- and 2,5-Disubstituted Furans via the CuI-Catalyzed Cycloisomerization of Alkynyl Ketones†

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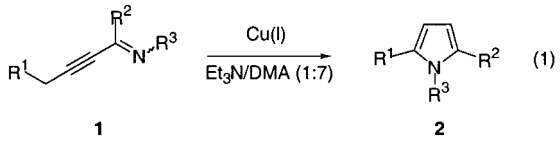
Received August 16, 2001

A mild, general, and efficient method for the synthesis of 2-monosubstituted and 2,5-disubstituted furans via the CuI-catalyzed cycloisomerization of alkynyl ketones was developed. It was demonstrated that furans containing both acid- and base-labile groups could be easily synthesized using this methodology. A plausible mechanism for this transformation is proposed.

Furan is a very important heterocyclic unit broadly found in natural[1,2] and biologically important[3] molecules and frequently used as building block in material science[4] and in organic synthesis.[1a,5] Two general approaches are commonly used for the preparation of substituted furans: the first, functionalization of existing furan-containing precursors by introduction of new substituents,[1a,b] and the second, formation of a new furan ring by cyclization of acyclic substrates.[1] The methods based on functionalization of preexisting furan precursors are not general. Thus, derivatization of furans via an electrophilic substitution motif is restricted due to the low stability of furans under strongly acidic conditions,[1a,6] whereas protocols involving metalation of furan derivatives followed by trapping of the furyl anion with electrophiles[1a,b] are limited to base-stable furan substrates and, in the case of alkylation, to primary electrophiles only. Among cyclization approaches, the classical acid-catalyzed cyclocondensation of 1,4-dicarbonyl compounds[1a] or related precursors[2c] still remains the most powerful method for the construction of a substituted furan ring. Here again, some limitations may arise in the case of acid-sensitive substrates. Recently, significant attention has been paid to the development of catalytic approaches, aiming at cycloisomerization of unsaturated acyclic precursors into furans, which can proceed under rather mild or neutral conditions.[1−4,7−9] It was reported that rhodium,[7a] silver,[2a,b,7b] and palladium[7c] assist efficient cycloisomerization of allenyl ketones into furans.[9] A few scattered reports describing the palladium-catalyzed cycloisomerization of the readily available, stable, and thus synthetically most attractive alkynyl ketones into furans are presented in the literature.[10] However, the reported methods are limited mostly to the synthesis of the aryl- or hetaryl-substituted furans and allows for the preparation of the furan derivatives either in moderate yields[10a,c] or accompanied with a trace to notable amounts of dimeric products.[10b] Herein we wish to disclose that various alkynyl ketones can be efficiently and selectively converted into the corresponding furans in the presence of catalytic amounts of CuI.

We have recently reported that alkynyl imines **1** undergo smooth transformation to pyrroles **2** in a Et_3N−DMA system (DMA = *N*,*N*-dimethylacetamide) in the presence of Cu(I) salts (eq 1).[11]



1 **2** (1)

Encouraged by the successful transformation **1** → **2**, we tested this cycloisomerization protocol for the synthesis of furans. It was found that the above-mentioned reaction conditions were efficient for the conversion of

† Dedicated to Professor Edmund Lukevics on the occasion of his 65th Birthday.

(1) For reviews, see: (a) Eberbach, W. Furan. In *Houben-Weyl*; Thieme: Stuttgart, 1994; E6a, Tail I, p 16. (b) Hou, X. L.; Cheung, H. Y.; Hon, T. Y.; Kwan, P. L.; Lo, T. H.; Tong, S. Y.; Wong, H. N. C. *Tetrahedron* **1998**, *54*, 1955. (c) Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2849.

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(3) See, for example: Brown, T. H.; Armitage, M. A.; Blakemore, R. C.; Blurton, P.; Durant, G. J.; Ganellin, C. R.; Ife, R. G.; Parsons, M. E.; Rawlings, D. A.; Slingsby, B. P. *Eur. J. Med. Chem*. **1990**, *25*, 217.

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(5) See, for example: Kobayashi, Y.; Nakao, M.; Biju Kumar, G.; Kishihara, K. *J. Org. Chem*. **1998**, *63*, 7505.

(6) For electrophilic functionalization of furan derivatives under mild two−phase conditions, see: Lukevics, E.; Ignatovich, L.; Goldberg, Y.; Polyak, F.; Gaukhman, A.; Rozite, S.; Popelis, J. *J. Organomet. Chem*. **1988**, *348*, 11.

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(10) (a) Sheng, H.; Lin, S.; Huang, Y. *Tetrahedron Lett*. **1986**, *27*, 4893. (b) Jeevandandam, A.; Narkunan, K.; Cartwright, C.; Ling, Y.-C. *Tetrahedron Lett*. **1999**, *40*, 4841. (c) Matsuo, K.; Sakaguchi, Y. *Heterocycles*, **1996**, *43*, 2553. (d) Trost, B. M.; Schmidt, T. *J. Am. Chem. Soc*. **1988**, *110*, 2301.

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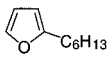
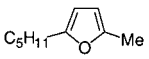
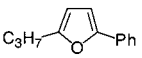
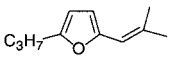
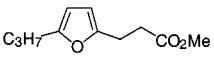
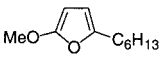
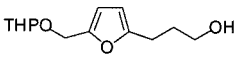
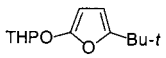
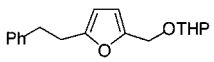
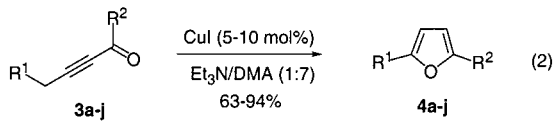
10.1021/jo010832v CCC: $22.00
Published on Web 11/22/2001

Table 1. Cu(I)-Catalyzed Synthesis of Furans 4

entry	alkynyl ketone **3**		temp (°C)	time (h)	furan **4**[a]	yield (%)[b]
	R^1	R^2				
1	H	Ph	80	3	 (a)	85
2	H	C_6H_{13}	130[c,d]	30	 (b)	63
3	C_5H_{11}	Me	100	27	 (c)	94
4	C_3H_7	Ph	100	16	 (d)	92
5	C_3H_7	$CH{=}CMe_2$	100[c]	43	 (e)	88
6	C_3H_7	$(CH_2)_2CO_2Me$	100	21	 (f)	91
7	MeO	C_6H_{13}	80	21	 (g)	78
8	$THPOCH_2$	$(CH_2)_3OH$	100	9	 (h)	88
9	THPO	t-Bu	100	22	 (i)	75
10	$Ph(CH_2)_2$	CH_2OTHP	100	4.5	 (j)	71

[a] The reactions were performed in 1 mmol scale in 7:1 solution of DMA−Et_3N (0.4 M) in the presence of 5 mol % of CuI, unless otherwise specified. [b] Isolated yield. [c] The reaction was carried out in the presence of 10 mol % of CuI. [d] A catalytic amount of triethylamine (10 mol %) was used; low yields of **4b** were obtained in the presence of excess triethylamine.

alkynyl ketones **3a**−**j** into the corresponding furans **4a**−**j**, as well (eq 2). In general, formation of furans **4** from

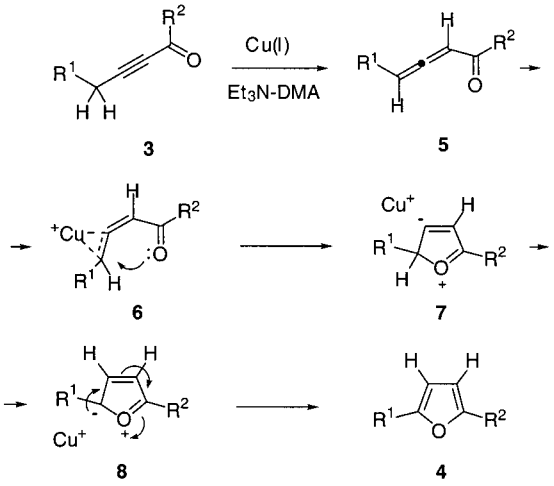


(2)

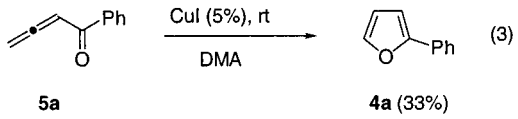
alkynyl ketones **3** (eq 2) appeared to be much easier than the analogous transformation **1** to **2** (eq 1): most of the reactions were completed in the presence of 5 mol % of CuI, whereas 30−50 mol % of copper was needed for the formation of pyrroles **2** (eq 1).[11] Thus, cycloisomerization of 1-phenylbut-2-yn-1-one (**3a**) in the presence of 5 mol % of CuI and excess triethylamine produced monosubstituted phenyl furan **4a** in 85% yield (Table 1). Formation of the monoalkylated furan **4b**, however, proceeded less smoothly: this compound was obtained in 63% yield only at a higher reaction temperature (130 °C) and in the presence of a catalytic amount (10%) of triethylamine. Cycloisomerization of alkynyl ketones **3c**−**j** proceeded with no complications, affording a variety of 2,5-disubstituted furans **4c**−**j** in good to excellent yields (Table 1, entries 3−10). Noticeably, this method allowed for easy introduction of various functional groups, such as an alkenyl (**4e**), alkoxy (**4g,i**), and bulky t-Bu-group (**4i**) directly into the furan ring. A remote ester group (**4f**), a THP-protected alcohol (**4h,j**), as well as an unprotected hydroxyl group (**4h**) have also been tolerated under these reaction conditions (Table 1).

We believe that the mechanism of the observed cycloisomerization of alkenyl ketones **3** into furans **4** (eq 2) is closely related to the previously proposed mechanism for the formation of pyrroles **2** from alkynyl imines **1** (eq 1).[11] First triethylamine−Cu(I)-catalyzed isomerization of alkynyl ketone **3** leads to the formation of allenyl ketone **5** (Scheme 1). Coordination of copper to the terminal double bond of allene (intermediate **6**) makes it more electrophilic and thus undergoes subsequent intramolecular nucleophilic attack by an oxygen lone pair to produce the zwitterionic intermediate **7**. The latter isomerizes via a deprotonation−protonation sequence[12] into its more stable isomer **8**, which finally transforms into furan **4**. The intermediates **6** and **7** are structurally close to those

Scheme 1



previously proposed for the Ag-assisted[7b] and the Pd-catalyzed[7c] cyloisomerization of allenyl ketones. To gain an additional support for the step **3** → **5**, the allenyl ketone **5a** was synthesized by an independent method[13] and subjected to the cycloisomerization reaction. As expected, **5a** appeared to be much more reactive compared to its propargyl precursor **3a** (Table 1, entry 1), affording 2-phenylfuran **4a** even at room-temperature albeit in 33% yield (eq 3).[14]



As a working hypothesis, this result can be rationalized in the following way. The Cu(I)-catalyzed and base-assisted propargyl−allenyl isomerization **3** to **5** is the slowest step of the sequence, which produces allenic intermediate **5** in very low concentrations. Allenyl ketone **5**, once formed, immediately undergoes fast sequential transformation into the stable furan derivative **4**[15] (Scheme 1).[16]

In conclusion, general and effective method for the synthesis of 2-monosubstituted and 2,5-disubstituted furans from easily available alkynyl ketones[17] in the presence of catalytic amounts of Cu(I) was developed. The generality of the method was demonstrated in the efficient preparation of furans possessing different functional groups, such as the sterically hindered t-Bu group, alkene moiety, alkoxy group directly attached to the furan ring, as well as a remote acid sensitive OTHP group, a base/nucleophile sensitive ester group, and an unprotected hydroxyl group.

(12) According to the deuterium labeling study performed for the cycloisomerization of allenyl imines, we ruled out possible involvement of "clean" hydrogen shifts and proposed a deprotonation−protonation sequence that resulted in a net migration of two hydrogens from the propargylic position into the heterocyclic ring.[11]

(13) Nagao, Y.; Lee, W.-S.; Kim, K. *Chem. Lett*. **1994**, 389.

(14) The reaction was carried out without triethylamine. Total decomposition of **5a** observed in the presence of triethylamine.

(15) Analogously, a catalytic amount of triethylamine was used to increase the yield of **4b** (Table 1, entry 2, note c). Most likely, an allenic intermediate **5b** (R^1 = H, R^2 = *n*-Hex) was produced in high concentration in the presence of excess triethylamine, which caused its rapid decomposition under harsh reaction conditions.

(16) This presumption is in agreement with the fact that allenic intermediate **5** has never been detected by GC−MS analyses of crude reaction mixtures.

Experimental Section

Instrumentation. NMR spectra were recorded on Bruker Avance DPX-400 (400 MHz) and on Brucker Avance DRX-500 (500 MHz) instruments. GC−MS analyses were performed on a Hewlett-Packard Model 6890 GC interfaced to a Hewlett-Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out by employing Merck silica gel (40−63 μm) or Aldrich aluminum oxide (activated, neutral, Brockmann I, ~150 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated silica gel plates (60 F_{254}) and neutral aluminum oxide plates (60 F_{254}). Alkynes, acyl chlorides, anhydrous solvents, and common reagents were purchased from Aldrich and Acros Organics.

Akynyl ketones 3a,d,e were prepared by the reaction of the corresponding alkynyl zinc chloride with benzoyl chloride or 3,3-dimethylacryloyl chloride in the presence of $Pd(PPh_3)_4$ (Negishi coupling) according to the known procedure.[17a] Spectral characteristics of known ketones **3a,d** were in agreement with the reported data for **3a**[17a] and **3d**.[18]

3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (quint, 1H, J = 1.1 Hz), 2.34 (t, 2H, J = 7.0 Hz), 2.18 (d, 3H, J = 1.0 Hz), 1.89 (d, 3H, J = 1.0 Hz), 1.52−1.56 (m, 2H), 1.38−1.43 (m, 2H), 0.90 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 157.3, 126.2, 92.7, 83.2, 29.8, 27.8, 22.0, 21.0, 18.7, 13.5; MS *m*/*z* (relative intensity) 163 (M^+ − 1, 4), 135 (M^+ − Et, 40), 79 (100); $C_{11}H_{16}O$.

2-Decyn-3-one 3b was prepared by the reaction of propynylzinc chloride with heptanoyl chloride according to the known procedure.[17a] Spectral data were in agreement with reported data.[19]

3-Decyn-2-one 3c was prepared by the reaction of octynyllithium with DMA according to the known procedure,[17a] spectral data were in agreement with the reported data.[20]

Alkynyl Ketones 3f−j: General Procedure. Alkynyl ketones **3f−j** were prepared by the reaction of the corresponding alkynylliythiums with the appropriate electrophiles (for the details, see Table 1). To a stirred solution of alkyne (5 mmol) in Et_2O (10 mL) (for compounds **3f,h,j**) or a mixture of Et_2O (5 mL) and THF (5 mL) (for compounds **3g,i**) at 0 °C was added a 2.5 M solution of BuLi in hexane (2.2 mL, 5.5 mmol) dropwise. The mixture was stirred for 0.5 h at 0 °C and then slowly added via cannula into a solution of the corresponding electrophile in Et_2O (10 mL) at −78 °C. The mixture was allowed to warm to 0 °C (in the cases **3f−i**) and quenched under vigorous stirring. In the case of **3j**, the mixture was kept for 1 h at −40 °C and allowed to warm to −10 °C before quenching. The organic layer was separated, washed with 5% aqueous NaCl, and dried over Na_2SO_4. The mixture was concentrated under reduced pressure, and the residue was chromatographed over a column of silica gel with EtOAc−hexane mixtures and for compound **3j** using Et_2O−benzene (1:20) as an eluent.

3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.87 (t, 2H, J = 6.8 Hz), 2.63 (t, 2H, J = 6.7 Hz), 2.36 (t, 2H, J = 7.0 Hz), 1.53−1.57 (m, 2H), 1.41−1.45 (m, 2H), 0.91 (t, 3H, J = 7.5

(17) For classical approaches toward alkynyl ketones, see: (a) Brandsma, L. *Preparative acetylenic chemistry*; Elsevier: New York, 1988. For the synthesis of alkynyl ketones from alkynyllithiums and esters in the presence of BF_3·Et_2O, see: (b) Yamaguchi, M.; Shibato, K.; Fujiwara, S., Hirao, I. *Synthesis* **1986**, 421. For the Cu(I)-catalyzed synthesis of alkynyl ketones from alkynes and acyl chlorides, see: (c) Ramachandran, P. V.; Teodorovic, A. V.; Rangaishenvi, M. V.; Brown, H. C. *J. Org. Chem*. **1992**, *57*, 2379. (d) Ito, H.; Arimoto, K.; Sensui, H.; Hosomi, A. *Tetrahedron Lett*. **1997**, *38*, 3977. (e) Sashida, H. *Synthesis* **1998**, 745. For Lewis acid assisted coupling of TMS−acetylenes with acyl chlorides, see: (f) Jones, G. E.; Holmes, A. B. *Tetrahedron Lett*. **1982**, *23*, 3203. (g) Robertson, J.; Burrows, J. N. *Synthesis*, **1998**, 63. (h) For the synthesis of alkynyl ketones from alkynyllithiums and Weinreb amides, see ref 10d.

(18) Kang, S.-K.; Lim, K.-H.; Ho, P.-S.; Kim, W.-Y. *Synthesis* **1997**, 874.

(19) Marshall, J. A.; Wang, X. *J. Org. Chem*. **1991**, *56*, 4913.

(20) Luo, F. -T.; Bajji, A. C.; Jeevanandam, A. *J. Org. Chem*. **1999**, *64*, 1738.

Table 2. Experimental Details for the Synthesis of Alkynyl Ketones 2f−j

	alkyne	electrophile (amount)	solution for quenching	product/ yield (%)
1	1-hexyne	methyl 4-chloro-4-oxobutyrate (10 mmol)	1% aq NH_3 (35 mL)	**3f**/48
2	methylpropargyl ether	heptanoyl chloride (10 mmol)	1% aq NH_3 (35 mL)	**3g**/46
3	4-tetrahydropyranyloxy-1-butyne	γ-butyrolactone (6 mmol)	sat. aq NH_4Cl(10 mL) + H_2O(20 mL)	**3h**/65
4	3-tetrahydropyranyloxy-1-propyne	pivalic anhydride (7.5 mmol)	sat. aq NH_4Cl (10 mL) + 1% aq NH_3 (10 mL)	**3i**/89
5	5-phenyl-1-pentyne	methyl tetrahydropyranyloxyacetate (7.5 mmol)	sat. aq NH_4Cl (10 mL) + H_2O (20 mL) + AcOH (0.54 mL)	**3j**/60

Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 172.6, 95.2, 80.4, 51.9, 40.0, 29.6, 27.8, 21.9, 18.6, 13.5; MS *m*/*z* (relative intensity) 196 (M^+, 0.5), 165 (M^+ − OMe, 3), 109 (100); $C_{11}H_{16}O_3$.

3g: (46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (s, 2H), 3.41 (s, 3H), 2.56 (t, 2H, J = 7.3 Hz), 1.64−1.68 (m, 2H), 1.27−1.33 (m, 6H), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 87.3, 85.4, 59.6, 58.0, 45.4, 31.5, 28.6, 23.9, 22.4, 14.0; MS *m*/*z* (relative intensity) 182 (M^+, 0.5), 152 (M^+ − Et, 2), 112 (67), 97 (100); $C_{11}H_{18}O_2$.

3h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64 (s, 1H), 3.85−3.95 (m, 2H), 3.54−3.64 (m, 3H), 3.44−3.54 (m, 1H), 2.62−2.77 (m, 4H), 2.26 (s broad, 1H), 1.88−1.92 (m, 2H), 1.74−1.87 (m, 1H), 1.64−1.74 (m, 1H), 1.44−1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 99.3, 91.9, 81.6, 65.0, 62.7, 62.0, 42.5, 30.9, 27.2, 25.7, 20.9, 19.7; $C_{13}H_{20}O_4$.

3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (t, 1H, J = 3.3 Hz), 4.41 (s, 2H), 3.79−3.85 (m, 1H), 3.49−3.59 (m, 1H), 1.64−1.85 (m, 2H), 1.49−1.64 (m, 4H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 97.0, 89.5, 82.9, 62.0, 53.8, 44.6, 30.0, 25.9 (×3), 25.2, 18.8; MS *m*/*z* (relative intensity) 167 (M^+ − *t*-Bu, 0.5), 124 (6), 85 (32), 57 (100); $C_{13}H_{20}O_3$.

3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.31 (m, 2H), 7.17−7.22 (m, 3H), 4.72 (t, 1H, J = 3.4 Hz), 4.34 (s, 2H), 3.85 (t, 1H, J = 9.2 Hz), 3.51−3.54 (m, 1H), 2.74 (t, 2H, J = 7.4 Hz), 2.38 (t, 2H, J = 7.0 Hz), 1.79−1.95 (m, 3H), 1.69−1.79 (m, 2H), 1.46−1.69 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 140.7, 128.5 (×4), 126.2, 98.3, 96.7, 79.1, 72.5, 62.0, 34.6, 30.1, 29.1, 25.3, 18.9, 18.4; MS *m*/*z* (relative intensity) 228 (1.5), 202 (M^+ − THP, 4), 171 (24), 128 (55), 104 (83), 85 (100); $C_{18}H_{22}O_3$.

Furans 4a−j: General Procedure. A mixture of propynyl ketone **3a−j** (1 mmol), CuI (9.6 mg, 0.05 mmol) (in cases of **3b,e**, 19 mg, 0.1 mmol), anhydrous DMA (2.2 mL) (in the case of **3b**, 2.5 mL), and Et_3N (0.3 mL) (in the case of **3b**, catalytic amount, i.e., 14 μL, 0.1 mmol) was stirred in a Wheaton microreactor (3 mL) under argon atmosphere (at the temperature given in Table 1) until the reaction was complete (monitored by GC−MS and TLC). The mixture was cooled, diluted (water, 15 mL), and extracted (pentane for volatile products **4a−c,e**, hexane for nonpolar products **4d,f,g,i,j**, ether for polar compound **4h**, 3 × 5 mL). Combined organic extracts were filtered (anhydrous Na_2CO_3), concentrated under reduced pressure, and chromatographed over a short column (silica gel; pentane as eluent for **4a−c,e**, hexane for **4d**, and mixtures EtOAc−hexane for **4f,h−j**). Compound **4g** appeared to be hydrolytically unstable on silica gel and was purified over a short column of Al_2O_3 with hexane as the eluent. Spectroscopic data for known products (**4a**,[21] **4b**,[22] **4c**,[20] **4d**[23]) were in agreement with the reported data.

4e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, 1H, J = 3.1 Hz), 6.02 (s, 1H), 5.97 (d, 1H, J = 3.2 Hz), 2.59 (t, 2H, J = 7.5 Hz), 1.98 (s, 3H), 1.89 (s, 3H), 1.67 (sext., 2H, J = 7.5 Hz), 0.97 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 152.0, 133.5, 114.5, 107.7, 106.2, 30.2, 26.9, 21.4, 20.0, 13.8; MS *m*/*z* (relative intensity) 164 (M^+, 23), 135 (M^+ − Et, 100); $C_{11}H_{16}O$.

4f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (d, 1H, J = 2.8 Hz), 5.84 (d, 1H, J = 2.8 Hz), 3.68 (s, 3H), 2.92 (t, 2H, J = 7.3 Hz), 2.63 (t, 2H, J = 7.0 Hz), 2.53 (t, 2H, J = 7.5 Hz), 1.58−1.65 (m, 2H), 0.94 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 155.5, 152.5, 106.0, 105.6, 52.0, 33.0, 30.4, 24.0, 21.8, 14.1; MS *m*/*z* (relative intensity) 196 (M^+, 15), 167 (M^+ − Et, 19), 123 (56), 107 (100). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.31; H, 8.22. Found: C, 67.40; H, 7.95.

4g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (dd, 1H, J_1 = 2.4, J_2 = 0.9 Hz), 4.99 (d, 1H, J = 3.0 Hz), 3.80 (s, 3H), 2.49 (t, 2H, J = 7.9 Hz), 1.52−1.65 (m, 2H), 1.24−1.37 (m, 6H), 0.88 (t, 3H, J = 6.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 146.8, 105.6, 79.6, 58.0, 32.0, 29.2, 28.4 (x2), 23.0, 14.5; MS *m*/*z* (relative intensity) 182 (M^+, 10), 111 (100); $C_{11}H_{18}O_2$.

4h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (d, 1H, J = 3.0 Hz), 5.92 (d, 1H, J = 3.2 Hz), 4.68 (t, 1H, J = 3.4 Hz), 4.58 (d, 1H, J = 12.8 Hz), 4.41 (d, 1H, J = 12.8 Hz), 3.87 (t, 1H, J = 7.4 Hz), 3.63 (t, 2H, J = 6.4 Hz), 3.44−3.54 (m, 1H), 2.68 (t, 2H, J = 7.5 Hz), 2.22 (s, 1H), 1.74−1.92 (m, 3H), 1.62−1.74 (m, 1H), 1.38−1.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 149.9, 110.2, 105.7, 97.1, 62.0, 61.8, 60.7, 30.9, 30.3, 25.4, 24.4, 19.2; MS *m*/*z* (relative intensity) 156 (M^+ − THP, 8), 138 (47), 55 (100); Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.96; H, 8.39. Found: C, 65.15; H, 8.34.

4i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (d, 1H, J = 3.0 Hz), 5.32 (t, 1H, J = 2.8 Hz), 5.26 (d, 1H, J = 3.3 Hz), 3.98 (td, 1H, J_1 = 13.9 Hz, J_2 = 2.8 Hz), 3.63−3.66 (m, 1H), 1.90−2.07 (m, 2H), 1.62−1.90 (m, 4H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.4, 102.4, 99.2, 84.2, 61.7, 32.3, 29.6, 28.9 (×3), 25.0, 18.0; MS *m*/*z* (relative intensity) 224 (M^+, 0.5), 209 (M^+ − Me, 1), 125 (22), 85 (100). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.60; H, 8.99. Found: C, 69.55; H, 8.86.

4j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.32 (m, 2H), 7.19−7.23 (m, 3H), 6.23 (d, 1H, J = 3.1 Hz), 5.94 (d, 1H, J = 3.1 Hz), 4.74 (t, 1H, J = 3.5 Hz), 4.66 (d, 1H, J = 12.8 Hz), 4.49 (d, 1H, J = 12.8 Hz), 3.94 (t, 1H, J = 7.4 Hz), 3.52−3.62 (m, 1H), 2.91−3.04 (m, 4H), 1.82−1.95 (m, 1H), 1.70−1.82 (m, 1H), 1.49−1.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 150.0, 141.2, 128.4 (×4), 126.1, 110.2, 106.0, 97.1, 62.0, 60.7, 34.3, 30.4, 30.1, 25.5, 19.3; MS *m*/*z* (relative intensity) 286 (M^+, 0.5), 184 (76), 141 (100). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.48; H, 7.75. Found: C, 75.23; H, 7.75.

Cycloisomerization of Allenyl Ketone 5a in DMA in the Presence of CuI. The mixture of CuI (9.6 mg, 0.05 mmol), ketone **5a**[13] (163 mg, 1.1 mmol), and anhydrous DMA (2.5 mL) was stirred under argon atmosphere at room temperature for 43 h and quenched as described above. Column chromatography (silica gel pentane as an eluent) gave 54 mg (33%) of 2-phenylfuran.[21]

Acknowledgment. The support provided by the National Science Foundation (CHE 0096889) is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR charts for compounds **4e** and **4g**. This material is available free of charge via Internet at http://pubs.acs.org

JO010832V

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