110 (23.7), 97 (100), 96 (30.5), 82 (13.6), 70 (32.6). Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.46; H, 12.21; N, 11.08.

2-Hexyl-6-methyl-2,3,4,5-tetrahydropyridine (6e): yield 136 mg (15%); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.0 Hz), 1.02-1.83 (14 H, m), 1.89 (3 H, d, J = 2.0 Hz), 2.08 (2 H, m), 3.25 (1 H, m); IR (neat) 1660, 1376 cm^{-1}; MS m/z (relative intensity) 181 (18.8, M^+), 166 (4.7), 152 (33.2), 138 (10.1), 124 (11.0), 110 (100), 97 (97.1), 96 (96.4), 82 (40.4). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.73. Found: C, 79.21; H, 13.04; N; 7.61.

5-Ethyl-2-pentyl-1-pyrroline (5f): yield 601 mg (72%); ^1H NMR ($CDCl_3$) δ 0.87 (3 H, t, J = 6.7 Hz), 0.93 (3 H, t, J = 7.0 Hz), 1.30-1.90 (8 H, m), 2.05 (2 H, m), 2.33 (2 H, t, J = 7.5 Hz), 2.45 (2 H, m), 3.88 (1 H, m); IR (neat) 1642, 1380, 1315 cm^{-1}; MS m/z (relative intensity) 166 (2.2, $M^+ - 1$), 152 (2.3), 138 (33.0), 124 (46.2), 111 (91.6), 110 (8.1), 96 (15.5), 82 (100). Anal. Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.65; N, 8.37. Found: C, 79.08; H, 12.84; N, 8.15.

6-Methyl-2-undecyl-2,3,4,5-tetrahydropyridine (6f): yield 527 mg (42%); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.5 Hz), 1.10-1.80 (24 H, m), 1.92 (3 H, d, J = 2.0 Hz), 2.08 (2 H, m), 3.25 (1 H, m); IR (neat) 1662, 1370 cm^{-1}; MS m/z (relative intensity) 251 (37.5, M^+), 236 (3.8), 222 (7.9), 208 (9.0), 194 (5.6), 180 (7.4), 166 (12.7), 152 (41.4), 138 (15.1), 124 (11.3), 110 (100), 97 (88.4). Anal. Calcd for $C_{17}H_{33}N$: C, 81.20; H, 12.23; N, 5.57. Found: C, 80.96; H, 12.25; N, 5.57.

Reaction of 4-Alkynylamine 2 in the Presence of Pd(II). 4-Dodecynylamine (**2a**, 500 mg, 2.76 mmol) was treated in refluxing acetonitrile (20 mL) in the presence of $PdCl_2$ (25 mg, 0.14 mmol, 5 mol %) for 8 h. The reaction mixture was diluted with ether (50 mL) and washed with a 1:1 mixture of aqueous NH_3 and brine (50 mL). The ethereal layer was dried (Na_2SO_4) and concentrated to give a mixture of 2-octyl-1-pyrroline (**5a**) and 6-heptyl-2,3,4,5-tetrahydropyridine (**6a**) in quantitative yield. NMR analysis of the product proved the ratio of **5a** and **6a** was 83:17: ^1H NMR ($CDCl_3$) δ 0.87 (3 H, t, J = 6.4 Hz), 1.20-1.48 (9.66 H, m), 1.59 (2 H, m), 1.85 (0.83 H, quint, J = 7.3 Hz), 1.86 (0.83 H, quint, J = 7.3 Hz), 2.13 (1.36 H, m), 2.32 (1.66 H, tt, J = 1.7, 7.6 Hz), 2.46 (1.66 H, tt, J = 1.7, 7.6 Hz), 3.54 (0.34 H, m), 3.80 (1.66 H, tt, J = 1.7, 7.3 Hz).

The same treatment of 1-methyl-4-undecynylamine (**2b**) as above gave a mixture of 2-heptyl-5-methyl-1-pyrroline (**5b**) and 6-hexyl-2-methyl-2,3,4,5-tetrahydropyridine (**6b**) quantitatively in the ratio of 80:20: ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.0 Hz), 1.23 (0.6 H, d, J = 6.8 Hz), 1.25 (2.4 H, d, J = 6.8 Hz), 1.20-1.75 (10.8 H, m), 2.13 (2 H, m), 2.36 (1.6 H, m), 2.50 (1.6 H, m), 3.45 (0.2 H, m), 4.06 (0.8 H, m).

Registry No. **1a**, 135469-67-9; **1a** alcohol, 55182-73-5; **1b**, 135469-68-0; **1b** alcohol, 135469-87-3; **1c**, 98551-99-6; **1c** alcohol, 14916-80-4; **1d**, 135469-69-1; **1d** alcohol, 135469-88-4; **1e**, 135469-70-4; **1e** alcohol, 10229-11-5; **1f**, 135469-77-1; **1f** alcohol, 135469-85-1; **2a**, 135469-71-5; **2a** alcohol, 92051-75-7; **2b**, 135469-72-6; **2b** ketone, 132716-18-8; **3a**, 112218-11-8; **3a** alcohol, 88109-70-0; **3b**, 135469-73-7; **3b** ketone, 135469-84-0; **3c**, 135469-74-8; **3c** alcohol, 41547-21-1; **3d**, 135469-75-9; **3d** alcohol, 135504-80-2; **3e**, 135469-76-0; **3e** alcohol, 69936-53-4; **3f**, 135469-78-2; **3f** alcohol, 135469-86-2; **4**, 135469-79-3; **4** alcohol, 37011-88-4; **5a**, 135469-80-6; **5b**, 128741-64-0; **5c**, 64319-86-4; **5d**, 700-91-4; **5f**, 135469-83-9; **6a**, 5832-27-9; **6b**, 135469-81-7; **6c**, 1604-01-9; **6e**, 135469-82-8; **6f**, 83019-11-8; $PdCl_2(MeCN)_2$, 14592-56-4; n-$C_5H_{11}C{\equiv}CH$, 628-71-7.

Synthesis of Substituted Furans by Palladium-Catalyzed Cyclization of Acetylenic Ketones

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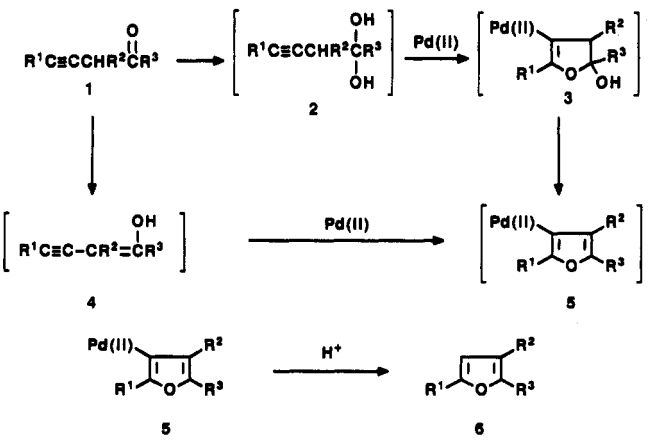
Palladium-catalyzed cyclization of β,γ-acetylenic ketones gives furans by intramolecular oxypalladation and subsequent protodemetalation. 3-Allylfurans were exclusively obtained by trapping the intermediate 3-furylpalladium species with allyl halides in the presence of 2,2-dimethyloxirane as a proton scavenger.

Substituted furans have been usually synthesized either by intramolecular reactions of 1,4-diketones or by the introduction of substituents to furan rings.[1-3] Various modifications of these methods have been extensively studied.[4-7] The recently reported Ta- or Nb-mediated coupling reaction of an alkyne, an aldehyde, and an isocyanide[8] as well as the Ag(I)-catalyzed cyclization of allenyl ketones[9] have opened novel methodologies for the synthesis of 2,3,5-trisubstituted furans. Danheiser et al. reported another synthesis of substituted furans by the reaction of allenylsilanes with acid chlorides in the presence of aluminum chloride.[10] Furans have also been prepared from acetylenic alcohols;[11-23] 2,5-dimethylfuran was prepared from 3-hexen-5-yn-1-ol,[11] and 2,5-di- or 2,3,5-trisubstituted furans were obtained from 2-methoxy-3-alkyn-1-ols by means of palladium catalysis.[24] A key step of the latter method is an intramolecular oxypalladation of the starting acetylenic alcohols to give 3-furylpalladium intermediates.

Scheme I

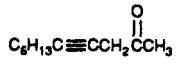
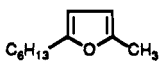
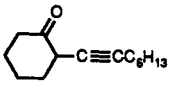
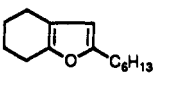
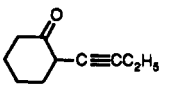
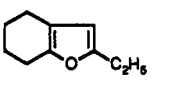


The same intramolecular oxypalladation was expected to proceed from an appropriate acetylenic ketone when an

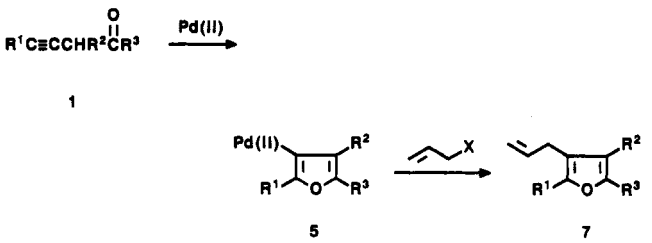
† On leave from Kyowa Yuka Co. Ltd., Yokkaichi, Mie, Japan.

0022-3263/91/1956-5816$02.50/0

Table I. Furans 6 from β,γ-Acetylenic Ketones 1

entry	acetylenic ketone	product	solvent	condition	yield (%)
1.			MeCN–H_2O	reflux 2 h	76
2.			MeCN	reflux 2 h	63
3.			THF–H_2O	reflux 3 h	45
4.			THF	reflux 3 h	79
5.			MeCN–H_2O	reflux 2 h	90
6.			MeCN	reflux 2 h	73
7.			THF–H_2O	reflux 1 h	26
8.			THF	reflux 1 h	76
9.			MeCN–H_2O	reflux 2 h	75
10.			MeCN	reflux 2 h	65
11.			THF–H_2O	reflux 1 h	8
12.			THF	reflux 1 h	74

Scheme II

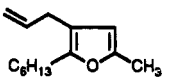
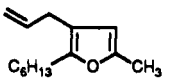
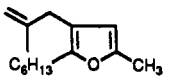
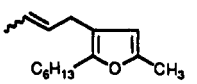
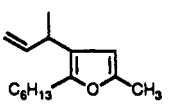


enol or a hydrate of the acetylenic ketone could react with palladium catalysts.[25] This paper describes in detail that furans are prepared from easily accessible β,γ-acetylenic ketones by either intramolecular oxypalladation–protodepalladation giving 2,5-disubstituted furans or oxypalladation–carbodepalladation with allyl halides affording 2,3,5-trisubstituted ones (Scheme I).[26]

Substituted furans **6** were formed in good to excellent yields from β,γ-acetylenic ketones **1** by treatment with palladium(II) catalysts in acetonitrile containing a few percent of water. Furans were also obtained in good yields by the reaction in anhydrous THF. In the former case, formation of furans could be explained by palladium(II)-catalyzed cyclization of either a hydrate **2** or an enol **4** of β,γ-acetylenic ketone **1**. In the later case, however, furan formation might proceed via cyclization of the enol **4**. Results are summarized in Table I.

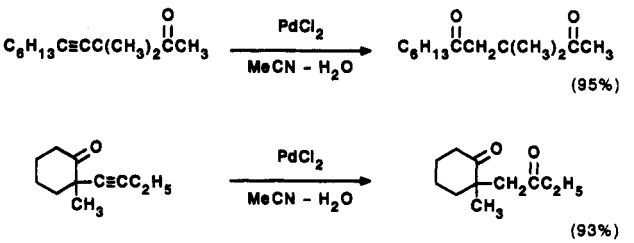
In the above-described transformations, furans were produced by the protonolysis of intermediary 3-furylpalladiums. During the sequence of transformations, the

Table II. 3-Allylfurans 7 from β,γ-Acetylenic Ketones 1

entry	allyl halide	product	yield[a] (%)	note
1			40[b]	*c*
2			70	*d*
3			67	*d*
4			83	*d,e*
5			70	*d*

[a] Isolated yield. [b] Determined by ^1H NMR. [c] 2-Methyloxirane as the proton scavenger; 2-hexyl-5-methylfuran (33%) was formed as byproduct. [d] 2,2-Dimethyloxirane as the proton scavenger; 2-hexyl-5-methylfuran was not detected. [e] *E*:*Z* = 6:4.

Scheme III



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(25) The Pd(II)-catalyzed synthesis of furans from β,γ-acetylenic ketones was preliminarily reported: Utimoto, K. *Pure Appl. Chem.* **1983**, *55*, 1845. A Pd(0) catalyst was also employed for the synthesis of furan although the yields were low. Sheng, H.; Lin, S.; Huang, Y. *Synthesis* **1987**, 1022.
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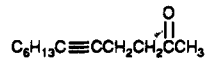
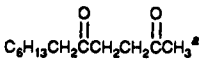
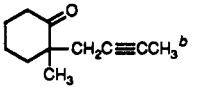
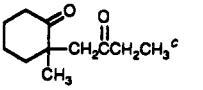
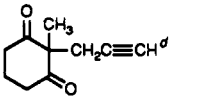
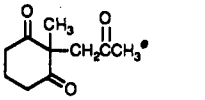
Table III. Regioselective Hydration of γ,δ-Acetylenic Ketones

entry	acetylenic ketone	diketone	solvent	condition	yield (%)
1			MeCN–H_2O	reflux 1 h	81
2			MeCN–H_2O	rt 30 min	90
3			THF–H_2O	rt 30 min	95
4			MeCN–H_2O	rt 30 min	93
5			THF–H_2O	rt 30 min	95

[a] Reference 32. [b] Reference 33. [c] Reference 34. [d] Reference 35. [e] Reference 36.

valency of palladium is unchanged and the Pd(II) species is regenerated. Since a 3-furylpalladium intermediate obtained from 2-methoxy-3-alkyn-1-ol has been utilized as reactive species,[24] reactions of the organopalladium intermediate **5** with electrophiles were examined. Allyl halides reacted exclusively on the γ-position with organopalladium intermediates to give 3-allylated 2,5-disubstituted furans. It is noteworthy that allylated furans were obtained exclusively when 2,2-dimethyloxirane was used as a proton scavenger. On the contrary, similar treatment of 2-methoxy-3-alkyn-1-ols gave considerable amounts of protonated furans in addition to the allylated ones (Scheme II).[24]

As starting materials, β,γ-acetylenic ketones **1** can be obtained in excellent overall yields by the coupling of 1-lithio-1-alkynes with oxiranes[26,27] followed by oxidation, this allylative cyclization reaction provides various types of furans from easily accessible 1-alkynes, oxiranes, and allyl halides (Table II).

On the other hand, in the case of β,γ-acetylenic ketones having no α-hydrogens, furan formation could not be expected, even though intramolecular oxypalladation of the corresponding hydrate is conceivable. Reaction of such acetylenic ketones with water in the presence of the Pd(II) catalyst gave 1,4-diketones under mild conditions (Scheme III).

γ,δ-Acetylenic ketones are also regioselectively hydrated via assistance of carbonyl oxygen,[28] but analogous treatment of α,β-acetylenic ketones with water resulted in the recovery of the starting material with formation of a small amount of tarry material. Examples of regioselective hydration of γ,δ-acetylenic ketones giving 1,4-diketones are summarized in Table III.

In conclusion, substituted furans were synthesized from corresponding β,γ-acetylenic ketones under the catalytic action of palladium(II) compound. Treatment of β,γ-acetylenic ketones with allyl halides in the presence of palladium(II) catalyst and 2,2-dimethyloxirane as a proton scavenger afforded 3-allylfurans exclusively. The reaction of γ,δ-acetylenic ketones or β,γ-acetylenic ketones with no α-hydrogens in aqueous acetonitrile gave corresponding 1,4-diketones by the catalysis of palladium(II) compounds.

Experimental Section

^1H NMR spectra were measured at 200 MHz. ^{13}C NMR spectra were measured at 100 MHz.

Preparation of 3-Alkyn-1-ols (General Procedure). To a THF–hexane solution of 1-lithio-1-alkyne prepared from 1-alkyne (10 mmol), *n*-BuLi (5.6 mL of 1.86 M solution in hexane, 10 mmol), and 10 mL of THF was added trimethylgallium (1 mL of 0.8 M solution in hexane, 0.8 mmol, 0.08 equiv to 1-alkyne) at 0 °C. To the reaction mixture maintained at 0 °C was added oxirane (12 mmol), and the whole was stirred at rt. The reaction mixture was worked up with brine and extracted with ether. The ethereal solution was washed (brine), dried (Na_2SO_4), and concentrated affording 3-alkyn-1-ol. The product was purified by column chromatography (silica gel, 33% EtOAc/hexane).

4-Undecyn-2-ol: yield 1.46 g (87%); ^1H NMR ($CDCl_3$) δ 0.89 (3 H, t, J = 6.7 Hz), 1.24 (3 H, d, J = 6.2 Hz), 1.20–1.60 (8 H, m), 2.15 (2 H, dt, J = 6.7, 2.4 Hz), 2.20 (1 H, br s), 2.32 (2 H, tt, J = 2.4, 6.6 Hz), 3.90 (1 H, tq, J = 5.8, 6.2 Hz); IR (neat) 3600–3000, 1150, 1080, 940 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.41; H, 12.22.

2-(1-Octynyl)cyclohexanol: yield 1.48 g (71%); ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, J = 6.5 Hz), 1.08–1.85 (15 H, m), 1.99 (2 H, m), 2.17 (2 H, br t, J = 6.2 Hz), 2.36 (1 H, d, J = 2.0 Hz), 3.37 (1 H, ddt, J = 2.0, 3.0, 9.5 Hz); IR (neat) 3600–3100, 1285, 1085 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.54, 11.84.

2-(1-Butynyl)cyclohexanol: yield 1.22 g (80%); ^1H NMR ($CDCl_3$) δ 1.16 (3 H, t, J = 7.5 Hz), 1.20–2.10 (9 H, m), 2.20 (1 H, m), 2.21 (2 H, dq, J = 2.0, 7.5 Hz), 3.41 (1 H, ddd, J = 2.5, 9.5, 9.5 Hz); IR (neat) 3650–3100, 1310, 1275, 1075 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.60; H, 10.85.

Preparation of β,γ-Acetylenic Ketones 1 (General Procedure).[29] The procedure for the preparation of 4-undecyn-2-one is representative. To a solution of 4-undecyn-2-ol (1.01 g, 6.0 mmol) in acetone (50 mL) was added Jones reagent[30] (prepared by dissolving 23.67 g of CrO_3 in 23 mL of concd sulfuric acid and diluting with water to a volume of 100 mL) dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and rt for additional 1 h. The excess reagent was reduced with 2-propanol (5 mL) at 0 °C and the whole was stirred at rt for 10 min. The reaction mixture was concentrated in vacuo, and the residue was washed with ether (30 mL) five times. The ether extract was dried (Na_2SO_4) and concentrated. Chromatographic purification (silica gel, 20% EtOAc/hexane) of the concentrate gave 4-undecyn-2-one (619 mg, 3.37 mmol, 62% yield). Similar oxidation of 2-(1-octynyl)cyclohexanol and 2-(1-butynyl)cyclohexanol gave 2-(1-octynyl)cyclohexanone (**1b**, 67% yield) and 2-(1-butynyl)cyclohexanone (**1c**, 58% yield), respectively. Acetylenic ketones **1** were soon used for the furan synthesis after the purification.

4-Undecyn-2-one (1a): yield 619 mg (62%); ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, J = 7.0 Hz), 1.25–1.75 (8 H, m), 2.23 (2 H, tt, J = 2.5, 7.1 Hz), 2.30 (3 H, s), 3.28 (2 H, t, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 18.8, 22.6, 28.5, 28.6, 28.8, 31.6, 35.0, 72.4, 85.1, 203.4; IR (neat) 1723, 1360, 1225, 1160 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.38; H, 10.95.

2-(1-Octynyl)cyclohexanone (1b): yield 664 mg (67%); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, J = 6.0 Hz), 1.18–2.15 (14 H, m), 2.21 (2 H, dt, J = 2.0, 5.0 Hz), 2.25 (1 H, m), 2.70 (1 H, m), 3.30 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 12.7, 12.9, 14.0, 19.1, 22.6, 28.3, 28.4, 31.6, 33.5, 33.7, 45.2, 80.3, 96.2, 189.1; IR (neat) 1710, 1120 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.31; H, 10.84.

2-(1-Butynyl)cyclohexanone (1c): yield 572 mg (58%); ^1H NMR ($CDCl_3$) δ 1.12 (3 H, t, J = 7.0 Hz), 1.20–1.35 (8 H, m), 2.20

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(2 H, dq, J = 2.5, 7.0 Hz), 3.40 (1 H, dt, J = 2.5, 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 12.7, 12.8, 23.4, 24.0, 33.6, 33.7, 45.0, 80.1, 96.0, 188.0; IR (neat) 1710, 1120 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.20; H, 9.65.

Preparation of Furans 6 from β,γ-Acetylenic Ketones 1 (General Procedure). Acetylenic ketone (1, 3 mmol) was dissolved in 3 mL of acetonitrile containing 0.3 mL of water or anhydrous THF. To this solution was added $PdCl_2(MeCN)_2$ (39 mg, 0.15 mmol, 0.05 equiv), and the whole was heated at reflux for 1–3 h. The reaction mixture was worked up with brine and extracted with ether. The ethereal solution was dried (Na_2SO_4) and concentrated. Column chromatography (silica gel, hexane) of the residue afforded the corresponding furan 6.

2-Hexyl-5-methylfuran (6a):[31] yield 393 mg (79%); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, J = 6.9 Hz), 1.25–1.42 (6 H, m), 1.63 (2 H, quintet, J = 6.0 Hz), 2.22 (3 H, s), 2.51 (2 H, t, J = 7.5 Hz), 5.70 (2 H, s); IR (neat) 1569, 1220, 1020 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.74; H, 10.92. Found: C, 79.66; H, 11.15.

2-Hexyl-4,5,6,7-tetrahydrobenzofuran (6b): yield 556 mg (90%); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, J = 6.0 Hz), 1.20–1.50 (6 H, m), 1.50–1.90 (6 H, m), 2.37 (2 H, t, J = 6.0 Hz), 2.52 (4 H, t, J = 8.0 Hz), 5.78 (1 H, s); IR (neat) 1560, 1438, 1219 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.34; H, 10.84.

2-Ethyl-4,5,6,7-tetrahydrobenzofuran (6c): yield 338 mg (75%); ^1H NMR ($CDCl_3$) δ 1.19 (3 H, t, J = 7.6 Hz), 1.62–1.90 (6 H, m), 2.33 (2 H, tt, J = 6.0, 2.0 Hz), 2.52 (2 H, t, J = 7.5 Hz), 5.78 (1 H, s); IR (neat) 1575, 1440, 1220 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.65; H, 9.50.

Preparation of 3-Allylfuran 7 from β,γ-Acetylenic Ketone 1 (General Procedure). To a solution of acetylenic ketone 9 (3 mmol) in allyl halide (10 equiv) and oxirane (50 equiv) was added $PdCl_2(MeCN)_2$ (0.05 equiv), and the reaction mixture was stirred at rt for 3 h. The product was purified by column chromatography (silica gel, hexane) of the concentrated reaction mixture.

3-Allyl-2-hexyl-5-methylfuran (7a): yield 433 mg (70%); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.1 Hz), 1.17–1.40 (6 H, m), 1.48–1.68 (2 H, m), 2.21 (3 H, t, J = 1.0 Hz), 2.50 (2 H, t, J = 7.5 Hz), 3.05 (2 H, dt, J = 6.6, 3.0 Hz), 4.96 (1 H, ddt, J = 3.1, 10.0, 3.0 Hz), 5.04 (1 H, ddt, J = 3.1, 16.9, 3.0 Hz), 5.78 (1 H, q, J = 1.0 Hz), 5.89 (1 H, ddt, J = 10.0, 16.9, 6.6 Hz); IR (neat) 3080, 1640, 1580, 995, 907 cm^{-1}; HRMS m/z calcd for $C_{14}H_{22}O$ 206.1669, found 206.1580. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.66; H, 10.79.

3-(2-Methyl-2-propenyl)-2-hexyl-5-methylfuran (7b): yield 442 mg (67%); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.1 Hz), 1.15–1.37 (5 H, m), 1.43–1.63 (3 H, m) 1.66 (3 H, s), 2.18 (3 H, s), 2.48 (2 H, t, J = 7.8 Hz), 2.96 (2 H, s), 4.70 (1 H, m), 4.74 (1 H, m), 5.47 (1 H, s); IR (neat) 3075, 1660, 890 cm^{-1}; HRMS m/z calcd for $C_{15}H_{24}O$: 220.1825, found 220.1769. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.73; H, 11.16.

3-(2-Butenyl)-2-hexyl-5-methylfuran (7c): yield 548 mg (83%); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.1 Hz), 1.18–1.42 (6 H, m), 1.48–1.61 (2 H, m), 1.69 (3 H, m), 2.20 (3 H, s), 2.50 (1.2 H, t, J = 7.5 Hz), 2.55 (0.8 H, t, J = 7.5 Hz), 2.98 (1.2 H, m), 3.05 (0.8 H, br d, J = 6.0 Hz), 5.48 (2 H, m), 5.77 (1 H, s) (E/Z mixture in a ratio of E:Z = 6:4); IR (neat) 3020, 1580, 970 cm^{-1}; HRMS m/z calcd for $C_{15}H_{24}O$ 220.1825, found 220.1753. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.63; H, 11.05.

3-(1-Methyl-2-propenyl)-2-hexyl-5-methylfuran (7d): yield 462 mg (70%); ^1H NMR ($CDCl_3$) δ 0.87 (3 H, t, J = 6.8 Hz), 1.21 (3 H, d, J = 7.2 Hz), 1.20–1.37 (6 H, m), 1.46–1.71 (2 H, m), 2.18 (3 H, s), 2.51 (2 H, d, J = 7.4 Hz), 3.28 (1 H, m), 4.96 (1 H, ddd, J = 1.9, 1.9, 10.3 Hz), 4.99 (1 H, ddd, J = 1.9, 1.9, 17.2 Hz), 5.79 (1 H, s), 5.92 (1 H, ddd, J = 6.4, 10.3, 17.2 Hz); IR (neat) 3080, 1640, 1580, 1262, 917, 800 cm^{-1}; HRMS m/z calcd for $C_{15}H_{24}O$ 220.1825, found 220.1772. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.47; H, 11.00.

Preparation of 3,3-Dimethyl-4-undecyn-2-one. To a THF solution of methyl iodide (1.14 g, 8 mmol, 2 equiv) and 4-undecyn-2-one (332 mg, 2 mmol) prepared as above was added 8 mL of 0.5 M THF–hexane solution of LDA (4 mmol, prepared from diisopropylamine (608 mg, 6 mmol) and butyllithium (4.4 mL of 1.35 M in hexane solution, 6 mmol) in 6.8 mL of THF) dropwise at −78 °C. The whole was stirred at −78 °C for 1 h and at rt for an additional 4 h. The reaction mixture was hydrolyzed with saturated aqueous NH_4Cl, extracted with ether, dried (Na_2SO_4), and concentrated. Chromatographic purification (silica gel, 20% EtOAc/hexane) of the residue gave 248 mg of 3,3-dimethyl-4-undecyn-2-one (64% yield). 2-(1-Butynyl)-2-methylcyclohexanone was prepared from 2-(1-butynyl)cyclohexanone by an analogous procedure in 60% yield.

3,3-Dimethyl-4-undecyn-2-one: ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, J = 6.6 Hz), 1.21–1.57 (8 H, m), 1.33 (6 H, s), 2.18 (2 H, t, J = 6.9 Hz), 2.34 (3 H, s); IR (neat) 2250, 1721, 1380, 1353, 1235, 1126 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.10; H, 11.62.

2-(1-Butynyl)-2-methylcyclohexanone: ^1H NMR ($CDCl_3$) δ 1.15 (3 H, t, J = 7.2 Hz), 1.26 (3 H, s), 1.48–1.78 (4 H, m), 1.99–2.32 (3 H, m), 2.20 (2 H, q, J = 7.2 Hz), 2.98 (1 H, ddd, J = 6.0, 13.2, 13.2 Hz); IR (neat) 1724, 1333, 1319, 1282, 1259, 1234, 1155, 1113, 1094, 1077, 1062, 982, 911, 863, 822 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.53; 9.79.

5-Dodecyn-2-one. Prepared by the reaction of 4-undecynoic acid with methyllithium (2.5 equiv) in ether: ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, J = 6.5 Hz), 1.18–1.58 (8 H, m), 2.12 (2 H, tt, J = 2.0, 7.2 Hz), 2.17 (3 H, s), 2.41 (2 H, tt, J = 2.0, 7.6 Hz), 2.64 (2 H, t, J = 7.6 Hz); IR (neat) 1719, 1364, 1162 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; 11.18. Found: C, 79.82; H, 11.44.

Hydration of Acetylenic Ketones (General Procedure). Hydrations of the acetylenic ketones were carried out by the same procedure used for furan synthesis from β,γ-acetylenic ketone. Thus, acetylenic ketone (1 mmol) was added to a solution of $PdCl_2(MeCN)_2$ (13 mg, 0.05 mmol, 5 mol %) in 5 mL of acetonitrile containing 0.5 mL of water, and the whole was stirred at rt for 30 min or heated at reflux for 1–3 h. After the acetonitrile was evaporated, the residue was diluted with ether and washed with 1:1 mixture of brine and aqueous NH_3. The ethereal solution was dried (Na_2SO_4) and concentrated to give the product. The ^1H NMR spectra showed that the products were pure and that no purification was needed.

3,3-Dimethyl-2,5-undecanedione: yield 201 mg (95%); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.5 Hz), 1.19 (6 H, s), 1.16–1.58 (8 H, m), 2.20 (3 H, s), 2.34 (2 H, t, J = 7.2 Hz), 2.37 (2 H, s); IR (neat) 1708, 1364, 1353, 1149, 1127, 1065 cm^{-1}. Anal. Calcd for $C_{13}H_{24}O$: C, 73.53; H, 11.39. Found: C, 73.82; H, 11.61.

Reaction of 3-Heptyn-2-one.[37] 3-Heptyn-2-one (220 mg, 2 mmol) was treated with 26 mg (0.1 mmol, 5 mol %) of $PdCl_2(MeCN)_2$ in 10 mL of refluxing acetonitrile containing 10% of water for 5 h. Workup of the reaction mixture as above gave mainly starting 3-heptyn-2-one along with small amount of tarry material.

Registry No. **1a**, 135645-94-2; **1b**, 135645-95-3; **1c**, 116373-17-2; **6a**, 5312-82-3; **6b**, 135645-96-4; **6c**, 57044-52-7; **7a**, 135645-97-5; **7b**, 135645-98-6; (*E*)-**7c**, 135645-99-7; (*Z*)-**7c**, 135646-02-5; **7d**, 135646-00-3; $PdCl_2(MeCN)_2$, 14592-56-4; 2-(1-octynyl)cyclohexanol, 135645-92-0; 2-(1-butynyl)cyclohexanol, 135645-93-1; 3,3-dimethyl-4-undecyn-2-one, 135646-01-4; 2-methyl-3-chloro-1-propene, 563-47-3; (*E*)-4-chloro-2-butene, 4894-61-5; 2-(1-butynyl)-2-methylcyclohexanone, 17782-34-2; 3,3-dimethyl-2,5-undecanedione, 135646-03-6; 3-heptyn-2-one, 26059-43-8; 3-chloro-1-propene, 107-05-1; 3-chloro-1-butene, 563-52-0; 4-undecyn-2-ol, 95061-41-9; 1-octyne, 629-05-0; 1-butyne, 107-00-6; propene oxide, 75-56-9; cyclohexene oxide, 286-20-4; 4-undecynoic acid, 54299-11-5; 5-dodecyn-2-one, 40657-58-7; (*Z*)-4-chloro-2-butene, 4628-21-1.

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