Articles

Palladium-Catalyzed Cyclocarbonylation of Terminal and Internal Alkynols to 2(5*H*)-Furanones

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A series of substituted alkynols, containing alkyl, phenyl, and vinyl groups at the acetylenic terminal, were found to undergo direct carbonylation to the corresponding substituted 2(5*H*)-furanones in 67−98% yield. This reaction requires catalytic quantities of $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mol %) and 1,4-bis(diphenylphosphino)butane (dppb) (8 mol %) in dichloromethane under an atmosphere of CO (600 psi) and H_2 (200 psi) at 95 °C for 36 h. Hydrogen is required for this reaction. Another bidentate ligand such as 1,3-bis(diphenylphosphino)propane, and a monodentate ligand such as PPh_3 or PCy_3, are equally effective for this reaction. Conjugated ene−ynols can also be carbonylated affording 3-alkenyl-2(5*H*)-furanones in good yield. However, double bond isomerization (*cis*−*trans*) occurred if an ene−ynol containing a *cis* olefinic substituent was used as the substrate. The cyclocarbonylation reaction is believed to proceed via an allenylpalladium intermediate, which is formed by initial insertion of Pd(0) into the C−O bond of the alkynol followed by a rearrangement.

The transition metal catalyzed carbonylation of propargyl alcohols and their derivatives has attracted considerable attention in recent years. The carbonylation of propargyl esters, halides, and phosphonates in the presence of various nucleophiles, such as alcohols, amines, and compounds containing activated methylene groups, has been extensively reviewed.[1] Previously we reported that the nickel-catalyzed carbonylation of alkynols can selectively furnish alkenoic acids under phase-transfer catalysis conditions,[2a,b] or dienoic acids using a hydrido(aqua)palladium complex.[3]

2(5*H*)-Furanone, or butenolide, comprises a structural moiety frequently present in biologically active natural products.[4] For instance *Annonaceous acetogenin*, isolated from a family of the tropical plant Annonaceous, displays interesting cytoytoxic activities against several cell lines.[5] It is known that butenolide can be prepared from propargyl alcohol via a sequence of transformations involving palladium-catalyzed carbonylation as one of the principal steps (Scheme 1). First reported by Stille and co-workers,[6a] propargyl alcohol was converted to iodoallyl alcohol by treatment with $LiAlH_4/I_2$, which was then cyclocarbonylated to butenolide using $Pd(PPh_3)_2Cl_2/K_2CO_3$ under 2 atm of carbon monoxide. Another approach is to first derivatize the propargyl alcohol as its ester, phosphonate ester, or other derivatives,[1] and then subject it to $Pd(PPh_3)_4$-catalyzed carbonylation in the presence of methanol to give the methyl ester of 2,3-dienoic acid. The ester was then hydrolyzed to the corresponding 2,3-dienoic acid which was subsequently transformed to butenolide with the use of either protonic acid (H^+)[7] or a Lewis acid such as Ag^+ ion.[8]

Thus far, there are few examples for the preparation of butenolides by direct incorporation of carbon monoxide into alkynols.[9] Indeed, an attempt to carbonylate internal alkynols to butenolides with $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ as the catalyst led to the formation of 2,3-dienoic acids as the major product in most cases.[10] In 1991, we reported the cyclocarbonylation reaction of terminal propargyl alcohols to 5,5-disubstituted 2(5*H*)-furanones—a direct synthesis of butenolide from propargyl alcohol—using $Pd(dba)_2$ and 1,4-bis(diphenylphosphino)butane (dppb) in DME at 150 °C for 48 h.[11] The reaction was not applicable to internal alkynols. We now report a modified procedure for this reaction which substantially extends its utility to internal alkynols with alkyl, phenyl, and vinyl units attached to one acetylenic carbon atom (eq 1).

Treatment of 2-methyl-4-butyn-2-ol (**1a**) with carbon monoxide (600 psi) and hydrogen (200 psi) in dichlo-

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[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1997.

(1) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2589.

(2) (a) Satyanarayana, N.; Alper, H. *Organometallics* **1991**, *10*, 804. (b) Zhou, Z. Z.; Alper, H. *Organometallics* **1996**, *15*, 3282.

(3) Huh, K. T.; Orita, A.; Alper, H. *J. Org. Chem.* **1993**, *58*, 6956.

(4) For review concerning the synthesis of butenolides, see: (a) Nagao, Y.; Dai, W.; Ochiai, M.; Shiro, M. *J. Org. Chem.* **1989**, *54*, 5211 and references cited therein. (b) Corey, E. J.; Cheng, X. M. In *The Logic of Chemical Synthesis*; John Wiley & Sons Inc: New York, 1989. (c) Knight, D. W. *Contemp. Org. Synth.* **1994**, *1*, 287.

(5) For review, see: Figadere, D. *Acc. Chem. Res.* **1995**, *28*, 359 and references cited therein.

(6) (a) Stille, J. K.; Cowell, A. *Tetrahedron Lett.* **1979**, 133. (b) Recently, the α,*β*-unsaturated iodo ketones were found to undergo carbonylation, affording *γ*-alkylidene butenolides: Coperet, C.; Sugihara, T.; Wu, G.; Shimoyama, I.; Negishi, E.-I. *J. Am. Chem. Soc.* **1995**, *117*, 3422 and references cited therein.

(7) For acid (H^+)-induced cyclization of 2,3-dienoic acids to butenolides, see: (a) Kresze, G.; Kloimstein, L.; Runge, W. *Liebigs Ann. Chem.* **1976**, 979. (b) Musierowicz, S.; Wroblewski, A. E. *Tetrahedron* **1977**, 1753.

(8) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367.

(9) An example of PdI_2/KI-catalyzed oxidative cyclocarbonylation of propargyl alcohols to α-methylene-*β*-lactone has been reported: Bonardi, A.; Costa, M.; Gabriele, B.; Salerno, G.; Chiusoli, G. P. *J. Chem. Soc., Chem. Commun.* **1994**, 1429. (b) Another study reported that acetylenes can be carbonylated under water-gas shift conditions to form butenolides using rhodium catalyst: Joh, T.; Doyama, K.; Onitsuka, K.; Shiohara, T.; Takahashi, S. *Organometallics* **1991**, *10*, 2493. (c) Alkynols were also reported to react with carbon monoxide and iodobenzene in the presence of transition-metal complex and carbon dioxide, affording 3(2*H*)-furanones: Inoue, Y.; Ohuchi, K.; Yen, I. F.; Imaizumi, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3518.

(10) Matsushita, K.; Komori, T.; Oi, S.; Inoue, Y. *Tetrahedron Lett.* **1994**, *35*, 5889.

(11) El-Ali, B.; Alper, H. *J. Org. Chem.* **1991**, *56*, 4099.

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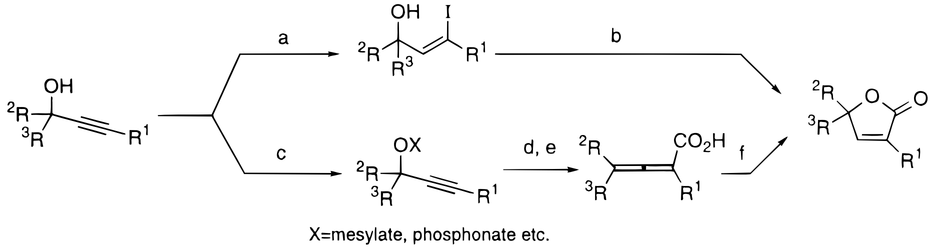
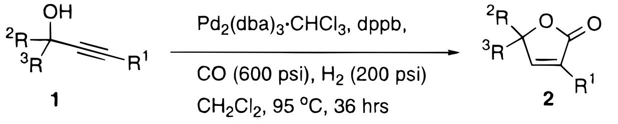
Scheme 1[a]



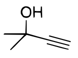
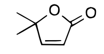
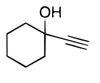
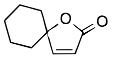
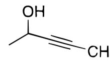
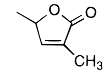
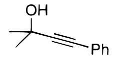
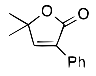
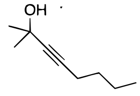
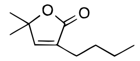
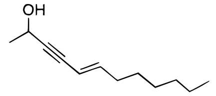
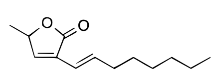
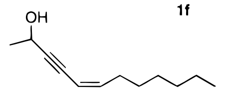
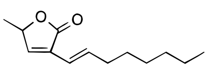
[a] (a) $LiAlH_4$, then I_2; (b) $Pd(PPh_3)_2Cl_2/K_2CO_3$, CO (2 atm); (c) mesyl chloride or diethyl chlorophosphate, base; (d) $Pd(PPh_3)_4$, CO, MeOH; (e) LiOH or BCl_3; (f) H^+ or Ag^+.



R_1 = H, alkyl, phenyl and vinyl
R_2, R_3 = H or alkyl (eq. 1)

romethane in the presence of catalytic quantities of $Pd_2(dba)_3 \cdot CHCl_3$ (4 mol %) and dppb (8 mol %) for 36 h at 95 °C afforded 5,5-dimethyl-2(5*H*)-furanone (**2a**) in nearly quantitative yield. Unlike the previously published procedure, this reaction requires a hydrogen atmosphere in order to obtain the butenolide in reasonable yield, as no butenolide was obtained without H_2 even at higher temperature (150 °C), and the substrate was recovered. The requirement for hydrogen was also encountered in the palladium-catalyzed cyclocarbonylation of allylphenols, anilines, and alcohols.[12] It is noteworthy that alkynols containing both terminal and internal C≡C bonds with alkyl, phenyl, and vinyl substituents attached to one of the acetylenic carbon atoms reacted with similar efficiency, affording 2(5*H*)-furanones in good to excellent yield (Table 1). By adopting the previous procedure, i.e. $Pd(dba)_2$/dppb, DME at 150 °C, no butenolide was obtained if 2-methyl-3-octyn-2-ol (**1e**) was used as the substrate, and partial decomposition of the alkynol was revealed by the GLC analysis of the crude reaction mixture. Other bidentate ligands such as 1,3-bis(diphenylphosphino)propane (dppp), or monodentate ligands like PPh_3 and PCy_3, can be used for this reaction, but 1,2-bis(diphenylphosphino)ethane is completely ineffective. This can be explained by the fact that CO insertion into a Pd−C bond occurs faster for those alkylpalladium diphosphine complexes containing a more flexible metal−ligand chelate ring.[13] Tertiary as well as secondary propargyl alcohols can be converted to the corresponding butenolides, but a primary alkynol, such as 2-butyn-1-ol, was unreactive under the typical carbonylation conditions. The choice of solvent was important as only dichloromethane or chloroform were useful for attaining the butenolide. The use of tetrahydrofuran, dimethoxyethane, benzene, or dimethylformamide as the solvent resulted in complete inhibition of the reaction or reduced butenolide production, or in case of DME as the solvent, substantial substrate decomposition was observed.

Table 1. Palladium-Catalyzed Cyclocarbonylation of Alkynols to 2(5*H*)-Furanones

Entry	Alcohol		2(5*H*)-Furanone		Yield % [a,b]
1		1a		2a	98
2		1b		2b	92
3		1c		2c	98
4		1d		2d	97
5		1e		2e	87 [c]
6		1f		2f	85 [d]
7		1g		2f	67 [d,e]

[a] Isolated yield. [b] Typical reaction condition: alcohol (1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.04 mmol), dppb (0.08 mmol), dry CH_2Cl_2 (10 mL), CO/H_2 = 600/200 psi at 95 °C, 36 h. [c] Sample contained α-*n*-butylidene-γ-lactone isomer; ratio of butenolide:γ-lactone = 4−4.5:1 as determined by ^{1}H NMR. The combined yield of the butenolide and the lactone was 97%. [d] Reaction was run for 48 h. [e] The *trans* isomer **2f** was formed as the major product, *trans*:*cis* ratio = 79:21 determined by ^{1}H NMR.

The $Pd_2(dba)_3$/dppb-catalyzed cyclocarbonylation of 2-methyl-3-octyn-2-ol (**1e**) to 3-*n*-butyl-5,5-dimethyl-2(5*H*)-furanone (**2e**) was accompanied by the formation of α-*n*-butylidene-γ-butyrolactone, probably *via* a C=C bond shift. Using ^{1}H NMR spectroscopy, the ratio of butenolide-to-γ-lactone was found to be 4−4.5:1 (determined by the integration ratio of the olefinic protons: [δ 6.95 (t, *J* = 1.5 Hz) for butenolide; δ 6.24 (t, *J* = 8 Hz) for γ-lactone]). The butenolide-to-γ-lactone isomerization became more pronounced when the reaction mixture was completely devoid of solvent. If the reaction mixture, with solvent completely evaporated, was left overnight at room temperature, the butenolide and γ-lactone were isolated in a 1:1 ratio as determined by ^{1}H NMR. The conjugated ene−ynol **1f** reacted with carbon monoxide to give 3-alkenyl-5-methyl-2(5*H*)-furanone **2f** in 85% isolated yield. If the isomeric ene−ynol **1g**, bearing a *cis* C=C linkage, was subjected to the carbonylation conditions, the butenolide **2f** containing a *trans* olefinic unit

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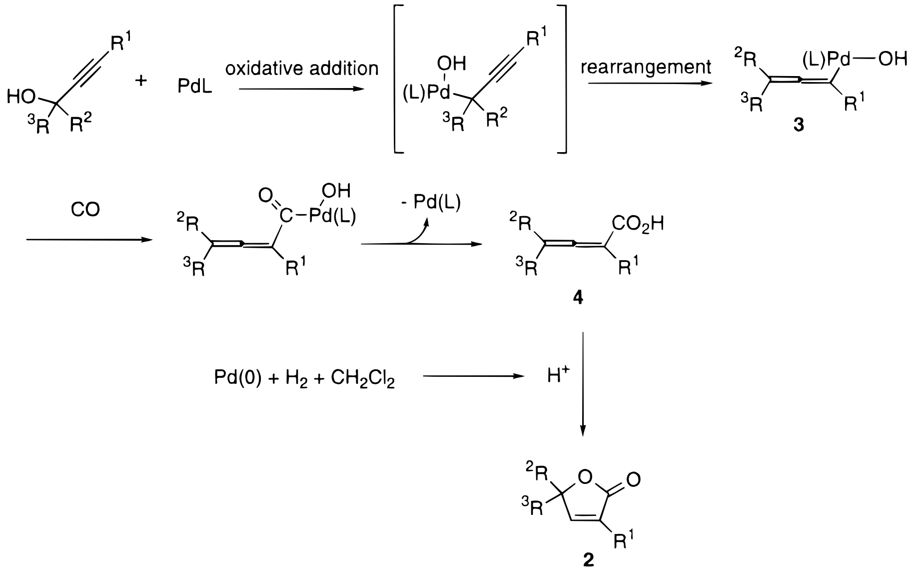
[12] (a) El-Ali, B.; Okuro, K.; Vasapollo, G.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 4264. (b) Yu, W.-Y.; Bensimon, C.; Alper, H. *Chem. Eur. J.* **1997**, in press. (c) Brunner, M.; Alper, H. *J. Org. Chem.* **1997**, submitted for publication.

[13] (a) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598. (b) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1992**, *430*, 357.

Scheme 2

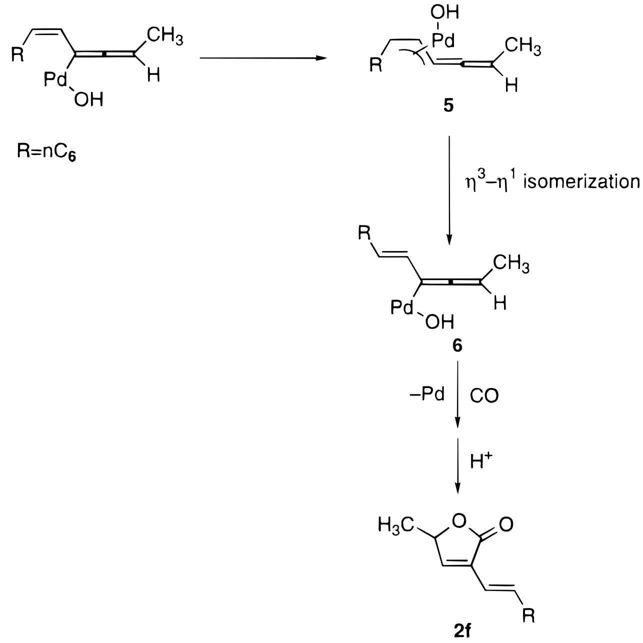


was formed as the major product with the *trans*:*cis* ratio being 79:21.

A possible mechanism for the cyclocarbonylation of alkynols is outlined in Scheme 2. Palladium(0) can undergo insertion into the C−O bond of the substrate followed by rearrangement to the allenylpalladium intermediate **3** (as proposed for allyl systems)[14]. Insertion of carbon monoxide and subsequent reductive elimination may lead to the 2,3-dienoic acid **4**. Trace quantities of acid present in the solvent can result in cyclization of **4** to give 2(5*H*)-furanone. Since only freshly dried CH_2Cl_2 was used for all reactions, and no transformation of substrate to butenolide was observed without the application of hydrogen gas, we assume that the protonic acid might have originated from the interaction between Pd(0), H_2, and CH_2Cl_2 under the reaction conditions, but the mechanism is unclear. Nevertheless, it is known that $CHCl_3$ reacts with H_2 and Pd(0) to generate H^+ as reported in the Pd/C-catalyzed hydrogenation of nitriles to amine hydrochlorides.[15] A control experiment performed under the standard carbonylation conditions, i.e. a CO/H_2 = 600/200 psi mixture, $Pd_2(dba)_3$/dppb in CH_2Cl_2, with added HCl (1 equiv *vs* Pd) using **1e** as the substrate resulted in complete consumption of the reactant in 8 h. However, only 38% (compared with 69% in the absence of HCl) of pure **2e** was isolated, and when the latter reaction was repeated in the absence of hydrogen, the yield of **2e** was 30%. These results indicate that hydrogen has several different roles in this reaction.

The *cis* → *trans* double bond isomerization in the cyclocarbonylation of the *cis* ene−ynol **1g** to **2f** may proceed via the π-allylpalladium complex **5** (Scheme 3). A similar intermediate has been proposed for the palladium-catalyzed reactions of 2,3-dienyl alcohols,[16] amines,[17] and esters.[18] The *trans* C=C bond could arise by η^3−η^1 isomerization of the π-allylpalladium complex **5** to the σ-allenylpalladium complex **6**, which then undergoes intramolecular cyclocarbonylation, affording the 2(5*H*)-furanone **2f**. Alternatively, the C=C bond isomerization might occur via a hydridopalladium intermediate involving a sequence of hydropalladation, C−C bond rotation, and then reductive elimination.

Scheme 3



In conclusion, $Pd_2(dba)_3 \cdot CHCl_3$ together with dppb is an excellent carbonylation system for the synthesis of 2(5*H*)-furanones from alkynols by reaction with carbon monoxide and hydrogen. This reaction represents an atom economical approach[19] to this class of synthetically useful compounds.

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(14) (a) Osakada, K.; Chiba, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1589. (b) Murahashi, S.-I.; Imada, I.; Taniguchi, Y.; Higashimura, S. *J. Org. Chem.* **1993**, *58*, 1538 and references cited therein.

(15) Serist, J. A. III; Logue, M. W. *J. Org. Chem.* **1972**, *37*, 335.

(16) Piotti, E. M.; Alper, H. *J. Org. Chem.* **1994**, *59*, 1956.

(17) Imada, Y.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1996**, *61*, 7982.

(18) (a) Kleijin, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 378. (b) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 203. (c) Nokami, J.; Maihara, A.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 5629.

(19) Recent examples of atom economical metal-catalyzed synthesis of butenolides include the following. (a) Ruthenium catalyzed Alder−ene reaction: Trost, B. M.; Muller, T. J. J. *J. Am. Chem. Soc.* **1994**, *116*, 4985. (b) Titanocene-catalyzed Pauson−Khand reaction of acetylenic ketones: Kablaoui, N. M.; Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 5818.

Experimental Section

Materials. Alkynols obtained from commercial source were used as received, or purified by vacuum distillation, if necessary, prior to use. Benzene, THF, 1,2-dimethoxyethane, and diethyl ether were dried and distilled from sodium/benzophenone ketyl under nitrogen before use. Dichloromethane for the cyclocarbonylation reaction was freshly distilled from CaH_2 under nitrogen. All other common solvents were used without purification. All chemicals were used as received. The acetone used for akynyllithium quenching was distilled from anhydrous K_2CO_3 prior to use. The vinyl bromide leading to the alkynols **1f**[20] and **1g**[21] and $Pd_2(dba)_3{\cdot}CHCl_3$[22] were prepared according to literature procedures.

General Procedure for the Preparation of Alkynols 1d and 1e. To a THF solution (15 mL) of phenylacetylene (10 mmol) [for **1d**]/1-hexyne (10 mmol) [for **1e**] was added *n*-BuLi (2.5 M in hexanes, 4.0 mL) at ice-cold temperature. The yellow solution was stirred at this temperature for at least 20 min. Acetone (ca. 0.8 mL) was then added, resulting in immediate decoloration. The solution was stirred for an additional 20 min, and then water (10 mL) was added. The product was then extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with brine (2 × 20 mL) and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the light yellow oily residue was purified by flash column chromatography using hexanes/diethyl ether = 2:1 as the eluant. The alcohols were further purified by vacuum distillation before use.

2-Methyl-4-phenyl-3-butyn-2-ol (1d): 83% yield; colorless oil; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 1.60 (s, 6H), 3.01 (s, 1H), 7.24−7.30 (m, 3H), 7.27−7.45 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$/TMS) δ 31.3, 65.4, 82.1, 93.9, 122.3, 128.0, 128.1, 131.5; HRMS (EI, 70 eV) calcd for $C_{11}H_{12}O$ [M^+] 160.088 82, found 160.089 21. Anal. Calcd for $C_{11}H_{12}O$: C, 82.45; H, 7.55. Found: C, 82.79; H, 7.69.

2-Methyl-3-octyn-2-ol (1e): 76% yield; colorless oil; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 0.91 (t, J = 7.2 Hz, 3H), 1.41−1.57 (m, 4H), 1.5 (s, 6H), 1.85 (s, 1H), 2.18 (t, J = 7.0 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$/TMS) δ 14.0, 22.5, 24.7, 28.5, 31.3, 58.5, 82.2, 84.7; HRMS (EI, 70 eV) calcd for $C_8H_{13}O$ [$M^+ - CH_3$] 125.0966, found 125.095 33. Anal. Calcd for $C_9H_{16}O$: C, 77.08; H, 11.51. Found: C, 77.13; H, 11.63.

General Procedure for the Preparation of Alkynols 1f and 1g.[23] To a mixture of vinyl bromide (3 mmol), 3-butyn-2-ol (3 mmol), and NEt_3 (5 mL) were added $Pd(PPh_3)_4$ (0.15 mmol) and CuCl (0.3 mmol) under an inert atmosphere. The mixture was stirred overnight at room temperature. The reaction mixture was then diluted with diethyl ether (20 mL) and filtered through Celite. The filter cake was washed with diethyl ether (ca. 30 mL), and the solvent was removed *in vacuo*. The oily residue was purified by chromatography using silica gel (eluant, hexanes/diethyl ether = 2:1). The alcohols were further purified by vacuum distillation.

***trans*-5-Dodecen-3-yn-2-ol (1f):** colorless oil; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 0.88 (br t, J = 7.1 Hz, 3H), 1.1−1.6 (m, 8H), 1.46 (d, J = 6.5 Hz, 3H), 2.13 (m, 3H), 4.63 (m, 1H), 5.45 (dd, J = 15.6, 1.5 Hz, 1H), 6.14 (dt J = 15.6, 7 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$/TMS) δ 14.0, 22.5, 24.3, 28.7, 31.5, 33.0, 58.7, 82.8, 89.3, 108.7, 145.5; HRMS (EI, 70 eV) calcd for $C_{12}H_{20}O$ [M^+] 180.151 41, found, 180.154 94. Anal. Calcd for $C_{12}H_{20}O$: C, 79.93; H, 11.19. Found: C, 80.15; H, 11.51.

***cis*-5-Dodecen-3-yn-2-ol (1g):** colorless oil; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 0.89 (br t, J = 6.6 Hz, 3H), 1.1−1.7 (m, 8H), 1.48 (d, J = 6.5 Hz, 3H), 2.12 (m, 1H), 2.32 (m, 2H), 4.68 (m, 1H), 5.48 (br d, J = 10.8 Hz, 1H), 5.91 (dt, J = 10.8, 7.3 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$/TMS) δ 14.1, 22.6, 24.4, 28.7, 30.2, 31.6, 58.8, 81.4, 95.6, 108.8, 121.8, 145.2; HRMS (EI, 70 eV) calcd for $C_{12}H_{20}O$ [M^+] 180.151 41, found 180.151 10. Anal. Calcd for $C_{12}H_{20}O$: C, 79.93; H, 11.19. Found: C, 80.07; H, 11.07.

Typical Procedure for the Palladium-Catalyzed Cyclocarbonylation of Alkynols. A mixture of the alkynol (1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.04 mmol), dppb (0.08 mmol), and anhydrous CH_2Cl_2 was reacted with carbon monoxide (600 psi) and hydrogen (200 psi) at 95 °C in a stainless steel autoclave for 36 h. After the autoclave was cooled to room temperature, the gases were released, and the crude reaction mixture was eluted through a plug of Florisil using CH_2Cl_2 as the eluant. The light yellow solution was evaporated to dryness using a rotary evaporator. The residue was then purified by chromatography with a short silica gel column using hexanes as the initial eluant, then with hexanes/ethyl acetate = 1:1 to elute the product from the column. The butenolide was further purified using Kugelrohr distillation.

2(5*H*)-Furanones **2a**, **2b**,[24] and **2c**[6a] are known compounds and had spectral data in accord with that of the literature.

The following butenolides are new.

5,5-Dimethyl-3-phenyl-2(5*H*)-furanone (2d): colorless crystals; mp 68.5−69.0 °C; $\nu_{C=O}$ = 1741 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 1.56 (s, 6H), 7.38−7.42 (m, 3H), 7.51 (s, 1H), 7.83−7.88 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$/TMS) δ 25.7, 83.4, 112.3, 127.1, 128.6, 129.2, 130.1, 152.9, 171.1; HRMS (EI, 70 eV) calcd for $C_{12}H_{12}O_2$ [M^+] 188.0837, found 188.081 94. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.56; H, 6.43. Found: C, 76.57; H, 6.58.

3-*n*-Butyl-5,5-dimethyl-2(5*H*)-furanone (2e): colorless oil; $\nu_{C=O}$ = 1735 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 0.93 (t, J = 7.3 Hz, 3H), 1.26−1.65 (m, 4H), 2.24 (t, J = 7.2 Hz, 2H), 6.95 (t, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$/TMS) δ 13.7, 22.2, 24.7, 25.7, 29.5, 84.2, 132.4, 153.0, 173.3; HRMS (EI, 70 eV) calcd for $C_{10}H_{16}O_2$[M^+] 168.115 03, found 168.116 31. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.38; H, 9.59. Found, C, 71.73; H, 9.64.

***trans*-3-(1-Octenyl)-5-methyl-2(5*H*)-furanone (2f):** colorless oil; $\nu_{C=O}$ = 1739 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$/TMS) δ 0.88 (br t, J = 6.6 Hz, 3H), 1.2−1.6 (m, 8H), 1.44 (d, J = 6.8 Hz, 3H), 2.15 (m, 2H), 5.05 (br q, $J \approx$ 6.9 Hz, 1H), 6.09 (dd, J = 15.9, 0.6 Hz, 1H), 6.81 (dt, J = 15.9, 8 Hz, 1H), 7.05 (d, J = 1.3 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$/TMS) δ 14.0, 19.1, 22.5, 28.7, 31.6, 33.4, 76.7, 118.2, 129.3, 138.7, 146.9, 172.1; HRMS (EI, 70 eV) calcd for $C_{13}H_{20}O_2$ [M^+] 208.146 33, found 208.146 62. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.95; H, 9.68. Found: C, 74.72; H, 9.88.

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(20) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

(21) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.

(22) Ukai, T.; Kawazura, H.; shii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

(23) Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.

(24) Tori, S.; Okamoto, T.; Tanaka, H. *J. Org. Chem.* **1974**, *39*, 2486.