Lactonization of Unsaturated Alcohols Catalyzed by Palladium Complexes under Neutral Conditions

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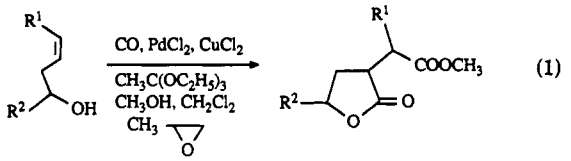
Received March 8, 1991

Secondary and tertiary allylic alcohols react with carbon monoxide in the presence of catalytic quantities of bis(dibenzylideneacetone)palladium(0) and 1,4-bis(diphenylphosphino)butane affording lactones in 45–92% isolated yields. α,β-Unsaturated acids are formed by isomerization and carbonylation of primary allylic alcohols. 2-(5*H*)-Furanones were isolated in yields of 60–80% when alkynols were employed as substrates for the cyclocarbonylation process.

The metal-catalyzed carbonylation of unsaturated substrates has been the subject of many investigations.[1,2] Recent examples include the cyclocarbonylation of alkynes to indanones catalyzed by cobalt carbonyl under water gas shift conditions,[3] and the palladium(II)-catalyzed dicarbonylation of homoallylic alcohols (3-buten-1-ols) and analogous 3-butyn-1-ols to lactone esters (eq 1).[4] The



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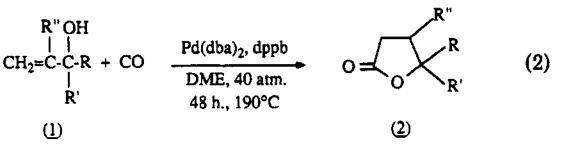
palladium reactions occur in the presence of cupric chloride, triethyl orthoacetate, and propylene oxide. Monocarbonylation of homoallylic alcohols to mixtures of five- and six-membered ring lactones takes place when the reaction is effected in the presence of acid and phosphine ligands, but without propylene oxide and triethyl orthoacetate.[5] One of us previously demonstrated that only five-membered ring lactones result when both oxygen and acid are utilized for the palladium chloride catalyzed carbonylation of homoallylic alcohols.[6] Allylic alcohols can also be converted to lactones using palladium chloride as the catalyst under acidic conditions and in the presence of oxygen as well as cupric chloride.[7,8]

We now describe a different palladium-based catalytic system for the lactonization of allylic alcohols under neutral conditions and in the absence of cupric chloride and oxygen. This methodology, which was first developed for formate ester reactions,[9] is also applicable to 1-alkyn-3-ols.

Results and Discussion

Treatment of 2-methyl-3-buten-2-ol (**1a**, R = R′ = CH_3, R″ = H) with carbon monoxide in 1,2-dimethoxyethane (DME) in the presence of catalytic quantities of bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] and 1,4-bis(diphenylphosphino)butane (dppb), for 48 h at 40 atm pressure and 190 °C, afforded 4,4-dimethyl-γ-butyrolactone (**2a**) in an isolated yield of 78% (eq 2). The ratio



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of substrate to palladium catalyst and added phosphine was 25:1:1. Only traces of **2a** resulted in the absence of dppb. Other bidentate phosphine ligands such as 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane are ineffective for this carbonylation process. Other palladium complexes can be used as catalysts, but the lactone is obtained in lower yield. Specifically, substitution of palladium acetate for $Pd(dba)_2$, under otherwise identical conditions, afforded the lactone in 60% yield, while **2a** was isolated in only 25% yield when tetrakis(triphenylphosphine)palladium(0) was employed as the catalyst.

This simple lactonization reaction is applicable to a variety of tertiary allylic alcohols containing alkyl, aryl, and olefinic groups attached to the hydroxyl-bearing carbon, with lactones obtained in good yields (see Table I for results). The olefinic unit can be mono- or 1,1-disubstituted but not internal since no reaction occurs in the latter case (e.g., 3-penten-2-ol). Secondary allylic alcohols behave in a similar manner. 3-Methyl-3-buten-2-ol affords nearly equal amounts of *cis*- and *trans*-3,4-dimethyl-γ-butyrolactone, showing that the reaction has no stereochemical control. An exception to the cyclocarbonylation reaction was found for the diallyl alcohol 1,4-pentadien-3-ol, which experienced carbonylation and isomerization to give 3,5-hexadienoic acid in modest yield. The primary allylic alcohols, allyl alcohol (**1n**) and 2-methyl-2-propen-1-ol (**1o**), isomerize and carbonylate to form α,β-unsaturated acids in excellent yields. The latter transformation has been observed previously, using palladium[10] or nickel[11] catalysts. The structures of the lactones and acids were determined by comparison of infrared, nuclear magnetic resonance, and mass spectral results with literature data as well as with authentic materials in some cases. New lactones were characterized on the basis of analytical and spectral data.

While a considerable amount of work has been done on the metal-catalyzed cyclization of homoalkynyl alcohols such as 3-butyn-1-ols,[4] comparatively little is known concerning the reaction of 1-alkyn-3-ols, which are acetylenic

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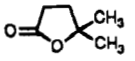
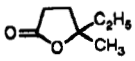
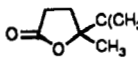
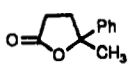
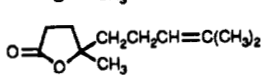
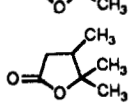
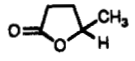
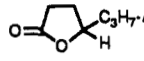
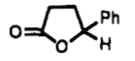
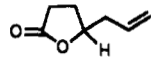
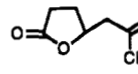
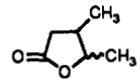
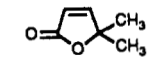
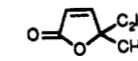
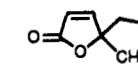
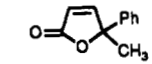
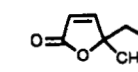
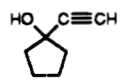
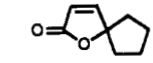
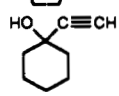
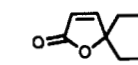
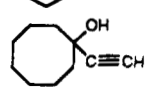
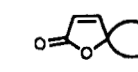
Table I. Cyclocarbonylation of Allylic Alcohols Catalyzed by $Pd(dba)_2$–dppb[a] (eq 2)

allyl alcohol		product		
structure	no.	structure	no.	yield[b] (%)
$CH_2{=}CHC(CH_3)(OH)CH_3$	1a		2a	78
$CH_2{=}CHC(OH)(C_2H_5)CH_3$	1b		2b	70
$CH_2{=}CHC(OH)(CH_3)C(CH_3)_3$	1c		2c	92
$CH_2{=}CHC(OH)(CH_3)Ph$	1d		2d	76
$CH_2{=}CHC(OH)(CH_3)CH_2CH_2CH{=}C(CH_3)_2$	1e		2e	80
$CH_2{=}C(CH_3)C(CH_3)OH$	1f		2f	51
$CH_2{=}CHC(OH)HCH_3$	1g		2g	74
$CH_2{=}CHC(OH)HC_3H_7\text{-}n$	1h		2h	65
$CH_2{=}CHC(OH)HPh$	1i		2i	74
$CH_2{=}CHC(OH)HCH_2CH{=}CH_2$	1j		2j	49
$H_2C{=}CHC(OH)HCH_2C(CH_3){=}CH_2$	1k		2k	52
$CH_2{=}C(CH_3)C(OH)HCH_3$	1l		2l	45[c]
$CH_2{=}CHC(OH)HCH{=}CH_2$	1m		2m	35
$CH_2{=}CHCH_2OH$	1n	$CH_3CH{=}CHCOOH$		93
$CH_2{=}C(CH_3)CH_2OH$	1o	$(CH_3)_2C{=}CHCOOH$		92

[a] Reaction conditions: alcohol (2.5 mmol), $Pd(dba)_2$ (0.1 mmol), dppb (0.1 mmol), DME (2.5 mL), CO (40 atm), 190 °C, 48 h. [b] Isolated yield. [c] 52/48 trans/cis.

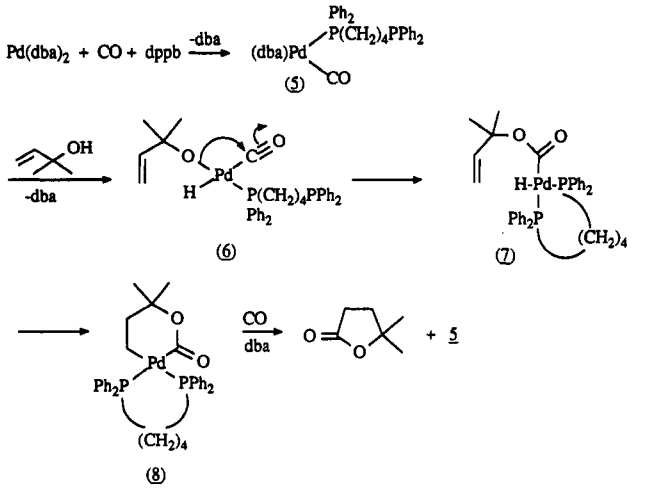
Table II. Synthesis of 2(5*H*)-Furanones by $Pd(dba)_2$–dppb-Catalyzed Carbonylation of Alkynols (eq 3)

alkynol		product		
structure	no.	structure	no.	yield[b] (%)
$(CH_3)_2C(OH)C{\equiv}CH$	3a		4a	60
$C_2H_5C(OH)(CH_3)C{\equiv}CH$	3b		4b	70
$(CH_3)_2CHCH_2C(OH)(CH_3)C{\equiv}CH$	3c		4c	62
$PhC(CH_3)(OH)C{\equiv}CH$	3d		4d	65
$CH_2{=}CHCH_2CH_2C(OH)(CH_3)C{\equiv}CH$	3e		4e	80
	3f		4f	80
	3g		4g	74
	3h		4h	65

[a] Reaction conditions: alkynol (2.5 mmol), $Pd(dba)_2$ (0.1 mmol), dppb (0.1 mmol), DME (2.5 mL), CO (20 atm), 150 °C, 48 h. [b] Isolated yield.

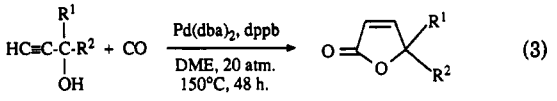
analogues of allylic alcohols. For examples, alkynols react with carbon monoxide and iodobenzene in the presence of a transition-metal complex and carbon dioxide, affording 3(2*H*)-furanones.[12] Carbon dioxide is essential for lac-

Scheme I



tonization, with an alkynylketo alcohol formed when the reaction is repeated without CO_2.[12,13]

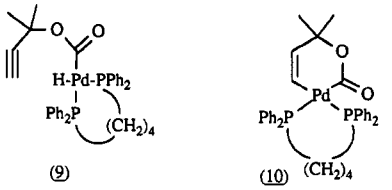
The $Pd(dba)_2$/dppb catalytic system is useful for the carbonylation of alkynols (3) to give 2(5*H*)-furanones (4) in good yield (Table II). Alkynols are somewhat more



reactive than allylic alcohols, as the reactions proceed in a satisfactory manner at lower pressure and temperature using the alkynol. No reaction occurs in the absence of dppb. Monocyclic and spirocyclic 2(5*H*)-furanones were isolated in reasonable yields by cyclocarbonylation of appropriate alkynols. Complimentary to the present methodology is the synthesis of 3,4-disubstituted 2(5*H*)-furanones by rhodium carbonyl ($Rh_4(CO)_{12}$,$Rh_6(CO)_{16}$) catalyzed carbonylation of internal alkynes including enynes.[14]

A possible mechanism for the conversion of allylic alcohols to lactones is outlined in Scheme I (illustrated for 2-methyl-3-buten-2-ol). Reaction of $Pd(dba)_2$ with dppb and carbon monoxide may give **5**.[9] The latter can undergo insertion into the oxygen–hydrogen bond of the allylic alcohol, affording **6**. Oxidative addition of water and methanol has been described for iridium(I) complexes.[15] Insertion of carbon monoxide into the palladium–oxygen bond (by ligand migration), with dppb bonded in the bidentate fashion, would give **7** (alkoxyplatinum complexes readily insert carbon monoxide).[16] Intramolecular addition of the palladium hydride to the double bond would form the metallocycle **8**. Conversion of **8** to the lactone would then occur by exposure to carbon monoxide and dba, with **5** being regenerated in the process. The ability of dppb to coordinate to palladium through one or both phosphorus atoms is probably key to success of this reaction.

The pathway in the case of alkynols is likely analogous to that of the allylic alcohols, with **9** and **10** as conceivable intermediates for the production of 2(5*H*)-furanones.



In conclusion, $Pd(dba)_2$–dppb is an effective catalytic system for the carbonylation of allylic alcohols and alkynols to γ-butyrolactones and 2(5*H*)-furanones under neutral conditions.

Experimental Section

General. ^1H NMR spectral data were obtained at 200 or 300 MHz. GC determinations were made with an OV-17 packed column.

Allylic alcohols, alkynols, and DME were commercial products and purified, if required, prior to use. Metal catalysts and phosphine ligands were purchased from commercial sources and were used as received. A 45-mL stainless-steel autoclave (Parr Instruments) was used for these reactions.

General Procedure for the Carbonylation of Unsaturated Alcohols. The allylic alcohol (2.5 mmol) or alkynol (2.5 mmol) was added into a 45-mL autoclave containing a solution of 0.0575 g (0.1 mmol) of $Pd(dba)_2$ and 0.0426 g (0.10 mmol) of dppb in 2.5 mL of DME. The autoclave was purged and then pressurized to either 40 (allylic alcohols) or 20 (alkynols) atm of CO. The reaction mixture was stirred at elevated temperature (190 °C for allylic alcohols, 150 °C for alkynols) for 48 h and then cooled to rt. The solution was filtered through Celite, and the filtrate was concentrated by rotary evaporation to give the cyclic compound. Purification was achieved by silica gel chromatography or by distillation.

γ-Butyrolactones. **2** (R = R′ = CH_3, R″ = H;[17] R = CH_3, R′ = C_2H_5, R″ = H;[18] R = CH_3, R′ = Ph, R″ = H;[18] R = R′ = R″ = CH_3;[17] R = CH_3, R′ = R″ = H;[7] R = *n*-C_3H_7, R′ = R″ = H;[7] R = Ph, R′ = R″ = H;[18] R = $CH_2CH{=}CH_2$, R′ = R″ = H;[18] R = R″ = CH_3, R′ = H[19]) are known compounds and had spectral properties in accord with the literature data.

The following lactones are new.

4-*tert*-Butyl-4-methyl-γ-butyrolactone (2c): IR ν(CO) 1768 cm^{-1}; NMR δ ($CDCl_3$) 0.91 (s, 9 H, $C(CH_3)_3$), 1.30 (s, 3 H, CH_3), 1.82 (m, 1 H, H-3), 2.18 (m, 1 H, H-3), 2.52 (m, 2 H, H-2); MS (*m/e*) 141 $(M - CH_3)^+$, 99 $(M - C(CH_3)_3)^+$. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.50; H, 10.38.

4-Methyl-4-(4-methyl-3-pentenyl)-γ-butyrolactone (2e): IR ν(CO) 1765 cm^{-1}; NMR δ ($CDCl_3$) 1.33 (s, 3 H, CH_3), 1.55 (s, 3 H, $(CH_3)_2C{=}$), 1.63 (s, 3 H, $(CH_3)_2C{=}$), 2.04–2.60 (m, 8 H, methylene protons), 5.10 (t, 1 H, J = 7.0 Hz, $CH{=}C(CH_3)_2$); MS (*m/e*) 182 $(M)^+$, 167 $(M - CH_3)^+$. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.91; H, 10.02.

4-(2-Methyl-2-propenyl)-γ-butyrolactone (2k): IR ν(CO) 1770 cm^{-1}; NMR δ ($CDCl_3$) 1.73 (s, 3 H, CH_3), 1.80–2.40 (m, 4 H, CH_2CH_2), 2.50 (m, 2 H, $CH_2C(CH_3){=}CH_2$), 4.50 (m, 1 H, CHOC(O)), 4.75 and 4.85 (2d, 2 H, J = 1.0 Hz, $CH_2{=}$); MS (*m/e*) 140 $(M)^+$, 85 $[M - CH_2C(CH_3){=}CH_2]^+$. Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.17; H, 8.84.

Unsaturated Acids. 3,5-Hexadienoic acid was identified by comparison of its spectral data with literature values,[20] while crotonic acid and 3-methyl-2-butenoic acid were characterized by comparison with commercial, authentic materials.

2(5*H*)-Furanones. **4** ($R^1 = R^2 = CH_3$;[21] $R^1 = CH_3$, $R^2 = C_2H_5$;[22] $R^1 = CH_3$, R^2 = Ph;[23] $R^1 = R^2 = (CH_2)_4$;[21] $R^1 = R^2 = (CH_2)_5$[21])

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are known compounds and had spectral properties in accord with literature data.

The following 2(5*H*)-furanones are new.

5-Methyl-5-(2-methylpropyl)-2(5*H*)-furanone (4c): IR ν(CO) 1765 cm^{-1}; NMR δ ($CDCl_3$); 0.90 (d, 6 H, J = 6.2 Hz, $(CH_3)_2CH$), 1.10 (m, 1 H, $CH(CH_3)_2$), 1.40 (s, 3 H, CH_3), 1.65 (d, 2 H, J = 6.9 Hz, CH_2), 6.00 and 7.35 (2d, 2 H, J = 5.6 Hz, CH=CH), 7.35 (d, 1 H, CH=); MS (m/e) 97 $(M - C_4H_9)^+$. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.01; H, 9.20.

5-(3-Butenyl)-5-methyl-2(5*H*)-furanone (4e): IR ν(CO) 1755 cm^{-1}; NMR δ ($CDCl_3$) 1.40 (s, 3 H, CH_3), 1.80-2.15 (m, 4 H, CH_2CH_2), 5.00 (m, 2 H, CH_2=), 5.72 (m, 1 H, CH=CH_2), 6.02 and 7.35 (2d, 2 H, J = 5.6 Hz, CH=CH); MS (m/e) 98 $(M - C_4H_6)^+$. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.75; H, 7.58.

5,5-Heptamethylene-2(5*H*)-furanone (4h): IR ν(CO) 1745 cm^{-1}; NMR δ ($CDCl_3$) 1.30-2.10 (m, 14 H, $(CH_2)_7$), 6.05 and 7.40 (2d, 2 H, J = 5.7 Hz, CH=CH); MS (m/e) 180 $(M)^+$. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.96; H, 9.04.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council and to British Petroleum for support of this research.

Registry No. **1a**, 115-18-4; **1b**, 918-85-4; **1c**, 3732-61-4; **1d**, 6051-52-1; **1e**, 78-70-6; **1f**, 10473-13-9; **1g**, 598-32-3; **1h**, 4798-44-1; **1i**, 4393-06-0; **1j**, 924-41-4; **1k**, 17123-61-4; **1l**, 10473-14-0; **1m**, 922-65-6; **1n**, 107-18-6; **1o**, 513-42-8; **2a**, 3123-97-5; **2b**, 2865-82-9; **2c**, 54796-80-4; **2d**, 21303-80-0; **2e**, 134359-15-2; **2f**, 2981-96-6; **2g**, 108-29-2; **2h**, 105-21-5; **2i**, 1008-76-0; **2j**, 134359-16-3; **2k**, 134359-17-4; *cis*-**2l**, 10150-95-5; *trans*-**2l**, 10150-96-6; **2m**, 29949-29-9; **3a**, 115-19-5; **3b**, 77-75-8; **3c**, 107-54-0; **3d**, 127-66-2; **3e**, 51193-99-8; **3f**, 17356-19-3; **3g**, 78-27-3; **3h**, 55373-76-7; **4a**, 20019-64-1; **4b**, 30336-19-7; **4c**, 110296-01-0; **4d**, 53774-21-3; **4e**, 134359-18-5; **4f**, 5732-90-1; **4g**, 4435-19-2; **4h**, 134359-19-6; $Pd(dba)_2$, 32005-36-0; dpph, 7688-25-7; CH_3CH=CHCOOH, 3724-65-0; $(CH_3)_2C$=CHCOOH, 541-47-9.

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Arylmagnesium Bromide Additions to 1-Tetralone-2-acetic Acid Followed by Catalytic Hydrogenolysis: Stereochemical Consequences[1a]

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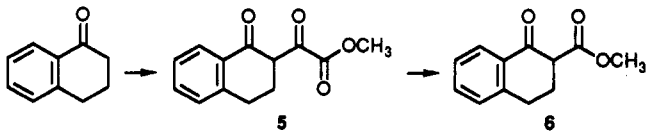
Received May 22, 1991

A Stork reaction route (**7** → **1b**) was utilized to synthesize 1-tetralone-2-acetic acid methyl ester (**1a**) from 1-tetralone. Addition of a 2'-(*o*-methoxyphenyl) magnesium bromide to this ketone followed by palladium-catalyzed hydrogenation of the intermediate cis lactones (**2**, verified by X-ray crystal structure determination of **2a**, Figure 1), afforded predominantly a 1,2-cis tetralin (**3**) accompanied by smaller yields of the corresponding 1,2-trans tetralin (**4**). The stereochemical consequences of this reaction sequence was unequivocally established by X-ray crystal structure elucidation of 1,2-cis methyl ester **3b** (Figure 2) and 1,2-trans carboxylic acid **4a** (Figure 3). Stereochemical assignments for the analogous diastereoisomeric sets **3c-f** and **4c-f** were obtained by high-field (400-MHz) ^{1}H and ^{13}C NMR correlations with the crystal structures. The overall reaction pathway illustrates a useful approach to 1,2-cis-alkylated tetralins and certain sterically hindered 1,2-trans-alkylated tetralins.

Some 36 years ago,[1] our interest in elucidating the structures of certain dienone-phenol rearrangement[2] products[3] led us to study the reaction between 1-tetralone-2-acetic acid methyl ester (**1a**) and the Grignard reagent from 2-bromo-4-methylanisole in order to open a route toward substituted benzo[*c*]phenanthrenes. Subsequent saponification, acidification, and hydrogenation (**1a** → **2** → **3** and/or **4**) resulted in a 1,2-cis-substituted tetralin **3** as major product. As summarized in the sequel, elucidation of the stereochemical consequences of this reaction sequence required modern instrumental techniques such as X-ray crystal structure determination and high-field (400-MHz) 2D ^{1}H and ^{13}C NMR, which were then not available. We now describe the successful completion of this early research.[1]

Several synthetic routes were evaluated for obtaining 1-tetralone-2-acetic acid methyl ester (**1a**). The following previously known procedure was employed to obtain the original supply of this ketone. Condensation of 1-tetralone[4a-c] with methyl oxalate, in the presence of freshly prepared sodium methoxide, led to glyoxalate (**5**).[4c] De-



5 **6**

carbonylation of the glyoxalate afforded 1,2,3,4-tetrahydro-2-carbomethoxy-1-oxonaphthalene (**6**).[5] Alkylation of ketone **6** with methyl bromoacetate gave 1,2,3,4-tetrahydro-1-oxo-2-naphthaleneacetic acid (**1b**) following hydrolysis and decarboxylation.[5,6] Yields in the latter pro-

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