Palladium(II)-Catalyzed Carbonylation of 3-Buten-1-ols and 3-Butyn-1-ols: An Efficient Synthesis of γ-Butyrolactones

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Palladium(II)-catalyzed dicarbonylation of 3-buten-1-ols (1) in the presence of propylene oxide and ethyl orthoacetate in methanol–dichloromethane under carbon monoxide at atmospheric pressure afforded α-[(methoxycarbonyl)methyl]-γ-butyrolactones (2) in good yields. This dicarbonylation reaction occurs via stereospecific cis addition. Under similar conditions, 4-(trimethylsilyl)-3-butyn-1-ols (**4a** and **4b**) undergo dicarbonylation to provide cis-dicarbonylated α-methylene-γ-butyrolactones (**5a** and **5b**, respectively). 4-Alkyl- and 4-aryl-3-butyn-1-ols (**4c–g**), on the other hand, undergo trans alkoxycarbonylation across the triple bond and selectively furnish *E* tetrasubstituted α-methylene-γ-butyrolactones (**6**).

Introduction

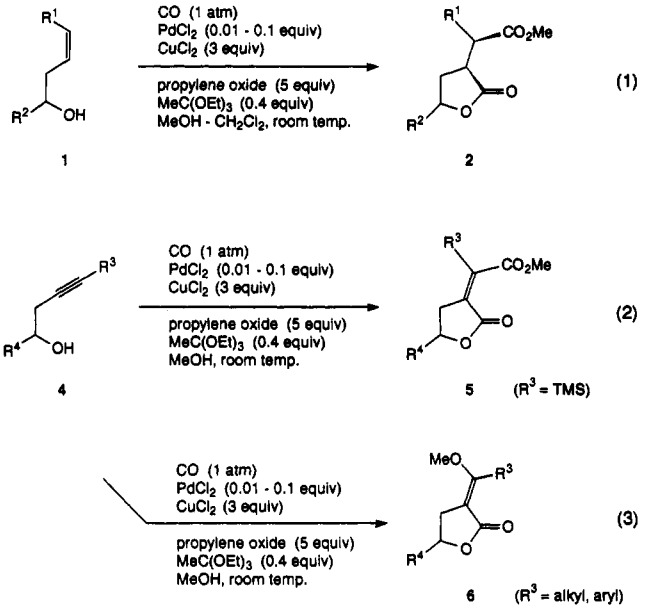
Transition-metal-catalyzed carbonylation is a very important process. Through this process carbon monoxide can be directly introduced to organic molecules as aldehydes, ketones, esters, amides, and other carbonyl functionalities. Although many transition metals are effective for carbonylation, particular attention has been paid to palladium, because of its versatile reactivity.[1]

Most studies on the palladium-catalyzed reactions are designed to utilize palladium(0) as the active catalytic species and hence the substrates are usually confined to those doubly functionalized with C–C double bond and some leaving groups (e.g., allyl acetate, aryl halides, vinyl triflate, etc.). Palladium(II)-catalyzed carbonylation seems to be potentially useful, since owing to its oxidizing ability, carbonylation could take place with nonfunctionalized olefins. However, such a reaction has been much less studied, because of the following apparent complexities of the catalytic system. First, in order to maintain the catalytic cycle, the palladium(0) species formed after one catalytic cycle must be reoxidized to palladium(II) by some appropriate oxidants without affecting the organic substrates and products. Second, palladium(II) often catalyzes double bond isomerization, and this may become a serious problem for the reaction of unsymmetrical olefins. Furthermore, the oxidation of carbon monoxide to carbonic acid derivatives (carbon dioxide, dialkyl carbonate) by Pd(II) may compete with the carbonylation of olefins in the presence of water or alcohol.[2]

Accordingly, most of the early studies on the Pd(II)-catalyzed carbonylation are concerned with simple, terminal olefins (e.g., ethylene[3] and styrene)[4] and/or cyclic olefins without substituents (e.g., cyclopentene).[5] This is not satisfactory from the standpoint of synthetic chemistry. Development of new methodology, capable of effecting carbonylation of complex olefins with various functionalities, is a worthwhile objective for organic chemists.

We describe the palladium(II)-catalyzed oxidative carbonylation of 3-buten-1-ols[6] and 3-butyn-1-ols (Scheme I).

Scheme I. Palladium(II)-Catalyzed Carbonylation of 3-Buten-1-ols (1) and 3-Butyn-1-ols (4)

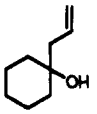
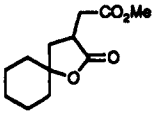
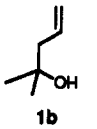
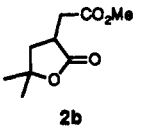
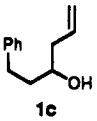
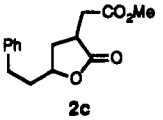
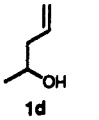
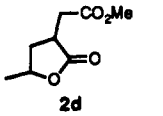
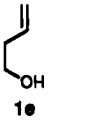
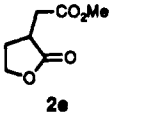


3-Buten-1-ols (1) undergo dicarbonylation to furnish α-[(methoxycarbonyl)methyl]-γ-butyrolactones (**2**) (eq 1). The reaction is stereospecific, and both carbonyls are introduced cis to the double bond. 3-Butyn-1-ols, depending on the kind of substituents on acetylenic termini (R^3), take a completely different course of reaction under the same conditions (eqs 2 and 3). When R^3 is trimethylsilyl group, cis dicarbonylation proceeds selectively (eq 2), while, when R^3 is alkyl or aryl group, trans alkoxycarbonylation takes place selectively (eq 3). The utility of the present reactions may be apparent from the ready availability of the starting materials with a wide structural variety[7] and the usefulness of γ-butyrolactone products as synthetic intermediates for many ways. The stereospecificity, the mild reaction conditions, and the general applicability to terminal and internal olefins and acetylenes as well as the large catalytic turnover numbers (10–100) should also be noted.

(1) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985; Chapter 8.
(2) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701.
(3) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1972**, *37*, 2034.
(4) Yukawa, T.; Tsutsumi, S. *J. Org. Chem.* **1969**, *34*, 738.
(5) (a) James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1806. (b) James, D. E.; Stille, J. K. *Ibid.* **1976**, *98*, 1810.
(6) A preliminary communication for carbonylation of 3-buten-1-ols: Tamaru, Y.; Hojo, M.; Yoshida, Z. *Tetrahedron Lett.* **1987**, *28*, 325.
(7) (a) Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1037 and references cited therein. (b) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870.

0022-3263/91/1956-1099$02.50/0

Table I. Palladium(II)-Catalyzed Dicarbonylation of 3-Buten-1-ols (1)[a]

entry	3-buten-1-ol	$PdCl_2$, mmol	additives: HCl quencher, mmol	additives: MeC-$(OEt)_3$, mmol	solvent $MeOH/CH_2Cl_2$, mL/mL	time, days	product	% yield (% conv)[b]
1		0.5	NaOAc, 5	0.4	3/6	2		25[c]
2		0.5	TMU, 5	0.4	3/6	1		77 (77)
3		0.1	PO, 5	0.4	3/6	1		94 (86)
	1a						**2a**	
4		0.1	PO, 3	0	3/6	1		26
5		0.1	PO, 5	0	3/6	1		47
6		0.1	PO, 5	0.4	3/6	1		72
	1b						**2b**	
7		0.1	PO, 5	0.4	3/6	1		97[d]
8		0.1	PO, 5	0.4	9/0	1		94 (35)[d]
	1c						**2c**	
9		0.1	PO, 5	0.4	3/6	1		82[d]
	1d						**2d**	
10		0.1	PO, 5	0.4	3/6	1		76
11		0.01	PO, 4	0.2	2/4	6		72
	1e						**2e**	

[a] Usual reaction conditions are as follows: a mixture of 3-buten-1-ol (1 mmol), $PdCl_2$ (indicated amount), $CuCl_2$ (3 mmol), an additive (TMU = tetramethyl urea, PO = propylene oxide) and a solvent in the presence or absence of ethyl orthoacetate (indicated amount) was stirred at an ambient temperature under 1 atm of carbon monoxide. [b] Yields refer to the isolated yields by means of column chromatography on silica gel. Unless otherwise specified, conversion is 100%. [c] 1-(1′-Propenyl)cyclohexanol was isolated in 56% yield. [d] Diastereomeric mixture was obtained in the ratio of ca. 4:6.

It may be interesting to compare the present reaction with the previously reported Pd(II)-catalyzed carbonylation of the longer carbon chain homologues, 4-penten-1-ols[8] and 5-hexen-1-ols.[9] In these cases the hydroxyl group served as a nucleophile toward the olefinic carbon activated by the coordination of Pd(II) and furnished 5- and 6-membered oxygen heterocycles (tetrahydrofuran-2-acetic acid and tetrahydropyran-2-acetic acid derivatives).

Results and Discussion

Palladium(II)-Catalyzed Synthesis of α-[(Methoxycarbonyl)methyl]-γ-butyrolactones from 3-Buten-1-ols (1). Synthetic and mechanistic studies on palladium(II)-catalyzed γ-butyrolactone synthesis have been done mainly by two groups. Alper[10] demonstrated that α-alkyl-substituted γ-butyrolactones could be produced by the carbonylation of 3-buten-1-ols (1) in moderate yields. For this hydrocarbonylation, the use of concentrated hydrochloric acid is essential. Norton and coworkers,[11] in their very fine and extensive work, have shown that palladium(II) catalyzes hydrocarbonylation of 3-butyn-1-ols (4) to furnish α-methylene-γ-butyrolactones in high yields. These studies are quite interesting in view of the difficulties associated with the palladium(II)-catalyzed reactions mentioned in the introduction. In fact, Stille[5] has shown in his pioneering work that simple olefins without substitutional auxiliaries undergo dicarbonylation to provide succinates. However, he has also noted that functionalized olefins give mixtures of products owing to isomerization of the double bond. For example, 3-buten-1-ol (1), the same substrate as that reported by Alper, provides a mixture of dicarbonylation products (dimethyl 2-vinylsuccinate, dimethyl 2-(2′-methoxyethyl)succinate, and dimethyl 2-(methoxymethyl)glutarate).[12]

The apparent difference of Alper's and Stille's results may be ascribed to the difference of the additives. The former utilized concentrated hydrogen chloride (acidic conditions) and the latter used sodium acetate (basic conditions). We have found that the use of propylene oxide as an additive (neutral conditions, vide infra) dramatically changes the reaction course and is very effective to promote the palladium(II)-catalyzed dicarbonylation of 3-buten-1-ols (Scheme I, eq 1). Results are summarized in Table I. The reaction resembles Stille's dicarbonylation of 3-butenol (1) with regard to the dicarbonylation of olefin; however, the cleanness of the present reaction, without accompanying olefin isomerization and providing α-[(methoxycarbonyl)methyl]-γ-butyrolactones (2) as a single product, is remarkable.

The effect of propylene oxide (PO) is apparent from the yields of 2 (entries 1–6). The role of PO for the selective production of 2 is not clear, but it apparently serves to quench hydrogen chloride and maintains the reaction

(8) Tamaru, Y.; Kobayashi, T.; Kawamura, S.; Ochiai, H.; Hojo, M.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 3207.

(9) (a) Semmelhack, M. F.; Bodurow, C. *J. Am. Chem. Soc.* **1984**, *106*, 1496. (b) Semmelhack, M. F.; Bodurow, C.; Baum, M. *Tetrahedron Lett.* **1984**, *25*, 3171.

(10) (a) Alper, H.; Leonard, D. *J. Chem. Soc., Chem. Commun.* **1985**, 511. (b) Despeyroux, B.; Alper, H. *Ann. N. Y. Acad. Sci.* **1984**, *415*, 148. (c) Fergusson, S. B.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1349. (d) Alper, H.; Woell, J. B.; Despeyroux, B.; Smith, D. J. H. *Ibid.* **1983**, 1270. (e) Alper, H.; Leonard, D. *Tetrahedron Lett.* **1985**, *26*, 5639. (f) Alper, H.; Hamel, N. *J. Am. Chem. Soc.* **1990**, *112*, 2803.

(11) (a) Samsel, E. G.; Norton, J. R. *Ibid.* **1984**, *106*, 5505. (b) Norton, J. R.; Shenton, K. E.; Schwartz, J. *Tetrahedron Lett.* **1975**, 51. (c) Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520. (d) Murray, T. F.; Norton, J. R. *Ibid.* **1979**, *101*, 4107.

(12) Stille, J. K.; Divakaruni, R. *J. Org. Chem.* **1979**, *44*, 3474.

conditions as neutral. Hydrogen chloride may be formed by 2 mol in every one catalytic cycle ($PdCl_2$ + 1 + CO + MeOH → Pd(0) + 2 + 2HCl). Based on the stoichiometry, only 2 mol of PO may be required. However, in fact, even by the use of 3 equiv of PO, the aqueous layer, obtained by washing the reaction mixture after completion of the reaction (entry 4), is acidic. On the other hand, by the use of 5 equiv of PO (entry 5), the mixture seems to be kept neutral all through the reaction, as judged from the neutral aqueous layer obtained after the similar extraction workup. The necessity of the use of excess propylene oxide may be due to some side reactions which produce extra HCl (e.g., oxidation of methanol and/or carbon monoxide[2] forming dimethyl carbonate and others). Some other kinds of typical bases were also examined. Tetramethylurea (TMU) showed marginal effectiveness with regard to the selectivity of the reaction (entry 2). However, in this case much larger amounts of $PdCl_2$ were required to draw the reaction to completion. By the use of sodium acetate, on the other hand, the expected lactone was isolated in only 25% yield (entry 1). The main reaction in this case was the isomerization of 3-butenol to 2-butenol (Table I, footnote *c*).

As an additive, the use of a small quantity of ethyl orthoacetate turns out to be effective to improve the yield (cf. entries 5 and 6). The expected role of this reagent is dehydration.[2] A small amount of water may be contained in the starting inorganics and/or produced by some side reactions. As a solvent a methanol–dichloromethane mixed solvent was found much superior to methanol alone (cf. entries 7 and 8).

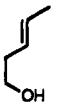
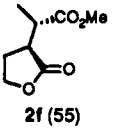
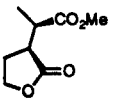
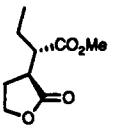
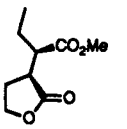
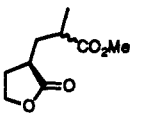
On the basis of these observations, several representative 3-buten-1-ols were subjected to dicarbonylation under the following optimized conditions. A mixture of 3-buten-1-ols (1) (1 mmol), $PdCl_2$ (0.1 mmol), $CuCl_2$ (3 mmol), propylene oxide (5 mmol), and ethyl orthoacetate (0.4 mmol) in methanol–dichloromethane mixed solvent (3–6 mL) was stirred under 1 atm of carbon monoxide at ambient temperature. The reaction was monitored with TLC and/or VPC.

The results obtained under the optimized conditions for 3-butenols with terminal and internal double bond are summarized in Tables I and II, respectively. As to the results in Table I, there are a few points worthwhile to note. The 3-butenols with a terminal double bond, irrespective of the structural variety, are reactive, and the reaction attains completion within 1 day at ambient temperature. The high reactivity may be exemplified by the result in entry 11, where only 0.01 equiv of catalyst is applied. In this case, the amounts of PO, ethyl orthoacetate, and the mixed solvent are also reduced relative to the substrate. Unfortunately the diastereoselectivity for the lactonization of 1-monosubstituted 3-butenols was only moderate (26/74 for **2c** and 38/62 for **2d**, entries 7–9), as determined by VPC.

Two pairs of cis–trans isomeric alcohols were examined (Table II). A single diastereomer was produced from each stereoisomer. That is, from trans alcohols (**1f** and **1h**) were obtained threo lactones (**2f** and **2h**, respectively) and from cis alcohols (**1g** and **1i**) erythro lactones (**2g** and **2i**, respectively). These stereochemical correlations clearly indicate that the present dicarbonylation stereospecifically proceeds in a cis addition.[5a]

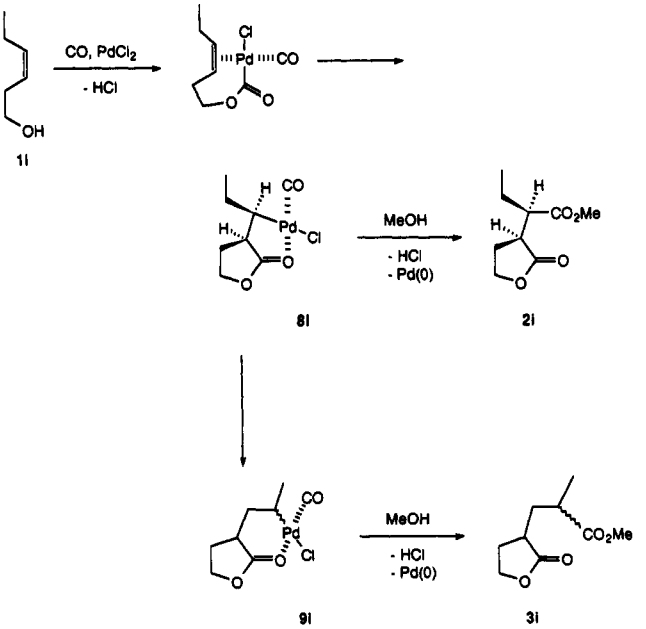
The reaction of *cis*-3-hexen-1-ol (**1i**) is exceptional with regard to its low reactivity and product selectivity. In this reaction α-[2-(methoxycarbonyl)propyl]-γ-butyrolactone (**3i**, 2:1 diastereomeric mixture) was produced as a minor product in addition to **2i** (entry 4) (**2i** (22%) and **3i** (28%) when conducted at ambient temperature for 2 days and then at 40 °C for 1 day).

Table II. Paladium(II)-Catalyzed Stereospecific Dicarbonylation of 3-Buten-1-ols (1)

entry	3-buten-1-ol	conditions[a]	product (% yield[b])
1	 **1f**	rt, 1 day	 **2f** (55)
2[c]	 **1g**	rt, 1 day	 **2g** (56)
3	 **1h**	rt, 2 days	 **2h** (63)
4	 **1i**	rt, 6 days	 **2i** (42)  **3i** (9)

[a] 3-Buten-1-ol 1 (1 mmol), $PdCl_2$ (0.1 mmol), $CuCl_2$ (3 mmol), propylene oxide (5 mmol), and ethyl orthoacetate (0.4 mmol) were stirred in methanol–dichloromethane mixed solvent (3–6 mL) under 1 atm of carbon monoxide. [b] Yields refer to the isolated yields by means of column chromatography on silica gel. [c] A mixture of **1g**:**1f** = 84:16 was used and a mixture of **2g**:**2f** = 85:15 was obtained.

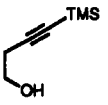
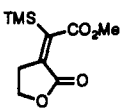
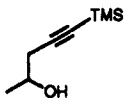
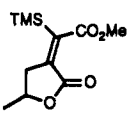
Scheme II. A Plausible Reaction Path for the Dialkoxycarbonylation of 3-Buten-1-ols (1)



1i 8i 2i 9i 3i

The most plausible reaction scheme for the present dicarbonylation of 1 is outlined in Scheme II, which is characterized by first lactonization followed by the methoxycarbonylation, and not vice versa. The anomaly observed for **1i** may be explained according to this scheme. The intermediate **8i**, formed by an intramolecular cis addition of (alkoxycarbonyl)palladium to the double bond, undergoes the second methoxycarbonylation with retention

Table III. Palladium(II)-Catalyzed Dicarbonylation of 3-Butyn-1-ols (4)[a]

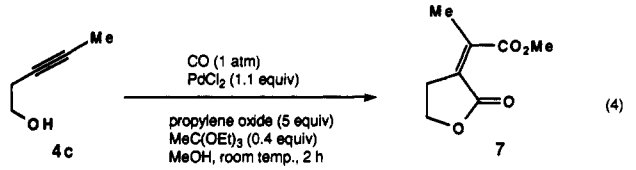
entry	3-butyn-1-ol	product (% yield[b])
1	 **4a**	 **5a** (81)
2	 **4b**	 **5b** (83)

[a] 3-Butyn-1-ol (4) (1 mmol), $PdCl_2$ (0.1 mmol), $CuCl_2$ (3 mmol), propylene oxide (5 mmol), and ethyl orthoacetate (0.4 mmol) were stirred in 9 mL of methanol under 1 atm of carbon monoxide at room temperature for 1 day. [b] Yields refer to the isolated yields by a short-path distillation of the crude reaction mixture under reduced pressure.

of configuration to form the usual cis dicarbonylation product **2i**. The steric repulsion in erythro **8i** formed from **1i** is such that the transformation of **1i** to **8i** may be sluggish and the thus formed **8i** might partly isomerize to **9i** via an elimination and addition of a hydrido palladium species.

An intramolecular oxycarbonylation of 1, a type of reaction reported by Semmelhack[9] and by us,[8] may be prohibited owing to the ring strain of the expected oxetane products.

The structure and stereochemistry of **2g** were determined by the comparison of its spectra with those of the sample prepared by hydrogenation of (*Z*)-α-[1-(methoxycarbonyl)ethylidene]-γ-butyrolactone (**7**), obtained by the stoichiometric dicarbonylation of 3-pentyn-1-ol (**4c**) (eq 4, vide infra). The IR and ^1H NMR spectra of both samples are superimposable in every respect.



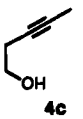
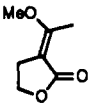
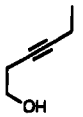
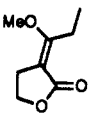
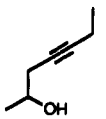
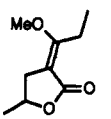
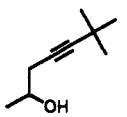
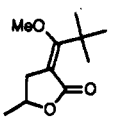
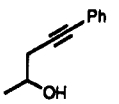
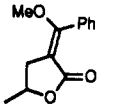
(4)

Palladium(II)-Catalyzed Carbonylation of 4-Substituted 3-Butyn-1-ols (4). 4-Substituted 3-butyn-1-ols were carbonylated under similar conditions applied to 3-buten-1-ols except for using methanol alone as the solvent. Interestingly, the reaction course dramatically changed depending on the kind of the C-4 substituents (Scheme I). When the substituent R^3 is trimethylsilyl group, cis dicarbonylation products **5** were obtained selectively in high yields (Table III). In those cases where R^3 is alkyl or aryl, on the other hand, trans methoxycarbonylation products **6** were produced selectively and in high yield (Table IV). The *E* structure of **5a** and **5b** was determined on the basis of the NOE experiments: a positive NOE between the TMS CH_3 and C_3-methylene protons and a negative NOE between the ester CH_3 and C_3-methylene protons. The *E* structure of **6e** was confirmed by the comparison of its spectral data with those of an authentic sample.[13]

The difference of the reaction course apparently cannot be attributed to a steric effect of the R^3 substituents, because alkyl groups, ranging from methyl to *tert*-butyl, give the same type of products. Hence, the change of the reaction course may be ascribed to the difference in the electronic effects of the silyl and alkyl groups. Reaction 2 is reminiscent of the regioselectivity in the hydroalumination[14] and alkylzincation[15] of silylacetylenes. In these reactions, the silyl group, owing to its electropositive nature, accelerates the addition of organometals in the direction to form the olefin with silyl and metal groups on the same carbon.

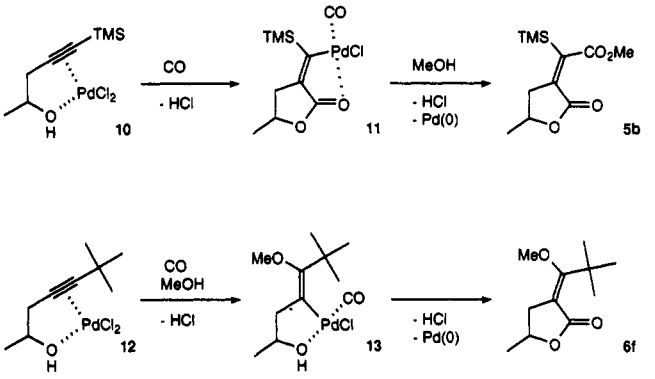
In reaction 2, (alkoxycarbonyl)palladium seems to add intramolecularly to the triple bond to form intermediate

Table IV. Palladium(II)-Catalyzed Methoxycarbonylation of 3-Butyn-1-ols (4)

entry	3-butyn-1-ol	conditions[a]	product (% yield[b])
1	 **4c**	rt, 4 h	 **6c** (94)
2[c]	4c	rt, 1 day	6c (89)
3	 **4d**	rt, 5 h	 **6d** (90)
4	 **4e**	rt, 6 h	 **6e** (83)
5	 **4f**	rt, 9 h	 **6f** (84)
6	 **4g**	rt, 18 h	 **6g** (89)

[a] 3-Butyn-1-ol (4) (1 mmol), $PdCl_2$ (0.1 mmol), $CuCl_2$ (3 mmol), propylene oxide (5 mmol), and ethyl orthoacetate (0.4 mmol) were stirred in 9 mL of methanol under 1 atm of carbon monoxide. [b] Yields refer to the isolated yields by a short-path distillation of the crude reaction mixture under reduced pressure. [c] The reaction was undertaken under the usual conditions except for using a reduced amount of $PdCl_2$ (0.01 mmol).

Scheme III. Plausible Reaction Paths for the Carbonylation of 3-Butyn-1-ols (4)



(13) Taskinen, E. *Acta Chem. Scand. Ser. B* **1985**, *B39*(6), 489.

(14) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383.
(15) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761.

11, which possesses geminal substitution of palladium and silyl groups (Scheme III). On the other hand, there is precedent for palladium(II)-assisted trans addition of heteroatom nucleophiles across triple bond.[16] Thus, reaction 3 might belong to this type of reaction, where the alkyl and aryl groups may participate in the formation of intermediate 13, owing to their ability to stabilize the carbonium ion α to them (Scheme III).

Both reactions 2 and 3 are highly stereoselective and may be useful for the stereoselective synthesis of tetrasubstituted α-methylene-γ-butyrolactones and their derivatives.

Interestingly, in sharp contrast to the general trend, **4c** afforded a dicarbonylation product **7** in 67% yield (eq 4) in the absence of $CuCl_2$ and by using a stoichiometric amount of $PdCl_2$. The *Z* structure of **7** was determined on the basis of a positive NOE between the olefinic CH_3 and C_3-methylene protons. This reaction, even in the presence of 5 equiv of propylene oxide, is acidic after completion of the reaction as judged from the aqueous layer obtained during extractive workup. Thus even in the presence of a sufficient amount of propylene oxide, HCl is not consumed in the absence of $CuCl_2$. This suggests that $CuCl_2$ effectively promotes the reaction of propylene oxide and HCl. The contrasting results in eqs 3 and 4 caused by the presence or absence of $CuCl_2$ indicate that $CuCl_2$ not only serves as an oxidant of Pd(0) but also plays a crucial role in the reaction course.[17]

Experimental Section

Melting points were determined in capillary tubes and were not corrected. Short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus. Boiling points are meant to refer to the oven temperatures. ^1H NMR spectra were determined at 60, 90, or 400 MHz, with tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined at 22.4 MHz. The purity of **2c,i**, **5a,b**, **6c–g**, and **7** was judged to be >90% by VPC, ^1H NMR, and/or ^{13}C NMR determinations. ^{13}C NMR spectra for **2c,i**, **6d–g**, and **7** and ^1H NMR spectra for **5a,b** and **6c** are given in the supplementary material.

Solvents and Reagents. Unless otherwise specified, the following solvents and reagents (reagent grade) were used without further purification: 3-buten-1-ols (**1d,e,f,h,i**), 3-butyn-1-ols (**4c–e**), propylene oxide, ethyl orthoacetate, carbon monoxide, palladium chloride, and cupric chloride. Tetrahydrofuran and diethyl ether were dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. Dichloromethane and methanol were distilled over CaH_2 under nitrogen atmosphere. 4-(Trimethylsilyl)-3-butyn-1-ol (**4a**),[11d] 5-(trimethylsilyl)-4-pentyn-2-ol (**4b**),[11d,18] and 5-phenyl-4-pentyn-2-ol (**4g**)[19] were prepared according to the reported procedures.

Procedure for Preparation of 3-Buten-1-ols (1a–c). To a solution of allylmagnesium bromide in diethyl ether (ca. 30 mmol/30 mL) was added 25 mmol of cyclohexanone, acetone, or dihydrocinnamaldehyde (distilled from K_2CO_3) at 0 °C, and then the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into saturated aqueous NH_4Cl at 0 °C. After extraction with Et_2O (3 × 15 mL), the extracts were washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). Removal of the solvent and distillation under a reduced pressure afforded 3-buten-1-ol (**1a**, **1b**, or **1c**) in quantitative yield. The structures of **1a**,[20] **1b**,[21] and **1c**[22] were determined by the comparison of the physical and spectral data in literatures.

(*Z*)-3-Penten-1-ol (1g). The titled compound was prepared by hydrogenation of 3-pentyn-1-ol (60 mmol, 5.16 g) in 30 mL of dry methanol in the presence of Lindlar catalyst (1.03 g) under 1 atm of H_2 at room temperature (2.1-L uptake of H_2). The reaction mixture was filtered with suction through a Celite pad on a funnel. The filter cake was washed several times with diethyl ether. This mixture was concentrated by a careful distillation of the solvents through a Vigreux-column and subjected to a bulb-to-bulb distillation at 100 °C (370 mmHg) (lit.[23] bp 70 °C (40 mmHg)) to afford 4.0 g (47 mmol, 78%, cis/trans = 84/16) of the known[23] 3-penten-1-ol: IR (film) 3350 (s), 1660 (w), 1440 (m), 1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$, D_2O added) δ 1.64 (d, *J* = 5.6 Hz, 3 H), 2.32 (br q, *J* = 7 Hz, 2 H), 3.63 (t, *J* = 6.6 Hz, 2 H), 5.40 (m, 1 H, coalescing to d, *J* = 10.7 Hz by irr at 2.32), 5.66 (m, 1 H, coalescing to d, *J* = 10.7 Hz by irr at 1.64); ^{13}C NMR ($CDCl_3$) δ 12.5, 30.3, 62.0, 126.0, 126.5; trans isomer ^{13}C NMR ($CDCl_3$) δ 17.4, 35.7, 61.9, 127.2, 127.5.

6,6-Dimethyl-4-heptyn-2-ol (4f). To a mixture of *n*-BuLi in hexane (20 mmol, 12.5 mL) and dry THF (30 mL) was added 3,3-dimethyl-1-butyne (20 mmol, 1.4 g) at 0 °C, and the mixture was stirred for 1 h. Propylene oxide (22 mmol, 1.3 g) was added to this mixture at −30 °C and stirred at room temperature overnight and then at 50 °C for an additional 5 h. The reaction was quenched by addition of 2 N HCl at 0 °C. After concentration of the mixture under a reduced pressure, the aqueous residue was extracted with ether (3 × 15 mL). The ethereal extracts were dried ($MgSO_4$) and concentrated to afford an oil, which was purified by column chromatography over silica gel (hexane–EtOAc gradient) to afford 1.61 g of **4f** (11.5 mmol, 58%): oil, bp 130 °C (60 mmHg); IR (film) 3350 (s), 1460 (s), 1360 (s), 1260 (s), 1115 (s), 1090 (s), 940 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 9 H), 1.22 (d, *J* = 5.9 Hz, 3 H), 1.33 (br s, 1 H), 2.31 (d, *J* = 5.9 Hz, 2 H), 3.85 (m, 1 H). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.01; H, 11.49.

General Procedure for Palladium(II)-Catalyzed Dicarbonylation of 3-Buten-1-ols (1). A 20-mL two-necked round-bottomed flask, containing a magnetic stirring bar, $PdCl_2$ (17.6 mg, 0.1 mmol), and $CuCl_2$ (404 mg, 3 mmol), was fitted with a serum-cap and a reflux condenser equipped at the top with a three-way stopcock connected to a balloon filled with carbon monoxide. The apparatus was purged with carbon monoxide by pumping-filling via the three-way stopcock. Dichloromethane (6 mL), ethyl orthoacetate (65 mg, 0.4 mmol), propylene oxide (290 mg, 5 mmol), 3-buten-1-ol (1 mmol), and methanol (3 mL) were introduced successively in this order into the flask via a syringe, and the mixture was stirred at ambient temperature for the period of time indicated in Tables I and II. After evaporation of the solvents, ethyl acetate was added, and the mixture was filtered with suction through a Celite pad on a funnel. The filter cake was washed several times with ethyl acetate, and the combined filtrates were washed with saturated aqueous $NaHCO_3$. After drying ($MgSO_4$) and evaporation of the solvent, the residue was subjected to purification by column chromatography over silica gel. The physical and spectral data of the products are as follows.

2-[(Methoxycarbonyl)methyl]-4,4-pentamethylene-γ-butyrolactone (2a): IR (film) 1760 (s), 1730 (s), 1195 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 0.95–1.73 (m, 10 H), 1.91 (dd, *J* = 12.5, 9.0 Hz, 1 H), 2.27 (dd, *J* = 17.6, 9.0 Hz, 1 H), 2.66 (d, *J* = 4.2 Hz, 1 H), 2.73–3.03 (m, 1 H), 3.36 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 22.4 (2 C), 24.7, 34.5, 35.7, 36.3, 38.0, 39.1, 51.6, 84.1, 171.4, 176.8; HRMS calcd for $C_{12}H_{18}O_4$ 226.1205, found *m/z* (relative intensity) 226.1223 (M, 68), 195 (49), 183 (91), 166 (100), 153 (67), 150 (65), 123 (41), 108 (57). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.82; H, 7.98.

1-(1′-Propenyl)cyclohexan-1-ol (the byproduct obtained in entry 1, Table I). The structure was confirmed by the comparison of spectral data with those of an authentic sample, prepared by a Grignard reaction (1-propenylmagnesium bromide and cyclo-

(16) Utimoto, K. *Pure Appl. Chem.* **1983**, *55*, 1845.
(17) For mechanistic investigations on the role of Cu(II) as an oxidant, see: (a) Hosokawa, T.; Uno, T.; Inui, S.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1981**, *103*, 2318. (b) Hosokawa, T.; Okuda, C.; Murahashi, S.-I. *J. Org. Chem.* **1985**, *50*, 1282. (c) Backvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335. (d) Heumann, A.; Backvall, J.-E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 207.
(18) Negishi, E.; Boardman, L. D.; Sawada, H.; Bagheri, V.; Stoll, A. T.; Tour, J. M.; Rand, C. L. *J. Am. Chem. Soc.* **1988**, *110*, 5383.
(19) Boweres, K. G.; Mann, J.; Walsh, E. B.; Howarth, O. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1657.
(20) Levina, R. Y.; Trakhtenberg, D. M. *J. Gen. Chem.* (*U.S.S.R.*) **1936**, *6*, 764; *Chem. Abstr.* **1936**, *30*, 6338.
(21) Dreyfuss, M. P. *J. Org. Chem.* **1963**, *28*, 3269.
(22) Wada, M.; Akiba, K. *Tetrahedron Lett.* **1985**, *26*, 4211.
(23) Blenderman, W. G.; Joullie, M. M. *J. Org. Chem.* **1983**, *48*, 3206.

hexanone): IR (film) 3370 (s), 1670 (w), 1640 (w), 1450 (s), 970 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (m, 11 H), 1.69 (d, J = 5 Hz, 3 H), 5.43–5.85 (m, 2 H).

2-[(Methoxycarbonyl)methyl]-4,4-dimethyl-γ-butyrolactone (2b): oil, bp 140 °C (0.2 mmHg); IR (film) 1765 (s), 1735 (s), 1290 (s), 1175 (s), 1135 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41 (s, 3 H), 1.49 (s, 3 H), 1.82 (t, J = 12.0 Hz, 1 H), 2.36 (dd, J = 12.0, 8.6 Hz, 1 H), 2.49 (dd, J = 15.9, 8.4 Hz, 1 H), 2.86 (dd, J = 15.9, 3.8 Hz, 1 H), 3.10–3.41 (m, 1 H), 3.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 26.7, 28.6, 34.5, 37.2, 40.9, 51.2, 81.8, 171.1, 176.2. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.79; H, 7.74.

2-[(Methoxycarbonyl)methyl]-4-(2-phenylethyl)-γ-butyrolactone (2c): a mixture of diastereomers (26/74); IR (film) 1765 (s), 1735 (s), 1265 (m), 1170 (s), 750 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70–2.30 (m, 3 H), 2.32–3.18 (m, 6 H), 3.70 (s, 3 H), 3.98–4.75 (m, 1 H, coalescing to a pair of s (4.42, 4.62) by irr at 2.05), 7.23 (s, 5 H); HRMS calcd for $C_{15}H_{18}O_4$ 262.1205, found m/z (relative intensity) 262.1197 (M, 14), 230 (10), 170 (23), 130 (82), 91 (100).

2-[(Methoxycarbonyl)methyl]-4-methyl-γ-butyrolactone (2d): a mixture of diastereomers (38/62); bp 135 °C (0.3 mmHg); IR (film) 1770 (s), 1740 (s), 1270 (m), 1180 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (d, J = 6.6 Hz, Me of one isomer), 1.44 (d, J = 6.1 Hz, Me of the other isomer), 2.07–3.29 (m, 5 H), 3.71 (s, 3 H), 4.37–4.99 (m, 1 H). Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.94; H, 6.95.

2-[(Methoxycarbonyl)methyl]-γ-butyrolactone (2e): bp 120 °C (0.3 mmHg); IR (film) 1765 (s), 1735 (s), 1265 (s), 1205 (s), 1155 (s), 1020 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75–2.31 (m, 1 H), 2.31–2.75 (m, 2 H), 2.75–3.19 (m, 2 H), 3.72 (s, 3 H), 4.06–4.56 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.2, 34.1, 35.6, 51.6, 66.3, 171.3, 177.7. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.42; H, 6.36.

***threo*-2-[1-(Methoxycarbonyl)ethyl]-γ-butyrolactone (2f)**: bp 140 °C (0.3 mmHg); IR (film) 1770 (s), 1735 (s), 1260 (m), 1165 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (d, J = 6.8 Hz, 3 H), 1.94–2.55 (m, 2 H), 2.80–3.26 (m, 2 H), 3.73 (s, 3 H), 4.04–4.57 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.9, 24.7, 38.8, 41.3, 51.3, 66.0, 174.1, 176.6. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.53; H, 7.27.

***erythro*-2-[1-(Methoxycarbonyl)ethyl]-γ-butyrolactone (2g)**: bp 120 °C (0.2 mmHg); IR (film) 1770 (s), 1735 (s), 1215 (s), 1165 (s), 1020 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (d, J = 7.1 Hz, 3 H), 2.09–2.46 (m, 2 H), 2.74 (dd, J = 9.5, 5.4 Hz, 1 H), 3.06 (dq, J = 5.4, 7.1 Hz, 1 H, coalescing to d, J = 5.4 Hz by irr at 1.35), 3.70 (s, 3 H), 4.25 (m, 1 H, coalescing to d, J = 9.3 Hz by irr at 2.35), 4.41 (m, 1 H, coalescing to d, J = 9.3 Hz by irr at 2.35); ^{13}C NMR ($CDCl_3$) δ 14.7, 25.2, 39.1, 41.8, 51.4, 66.0, 173.6, 176.9. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.73; H, 7.10.

***threo*-2-[1-(Methoxycarbonyl)propyl]-γ-butyrolactone (2h)**: bp 150 °C (0.6 mmHg); IR (film) 1775 (s), 1735 (s), 1270 (s), 1220 (s), 1160 (s), 1025 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3 H), 1.36–1.89 (m, 2 H), 2.15 (m, 1 H, coalescing to d, J = 12.7 Hz by irr at 4.22), 2.36 (m, 1 H, coalescing to d, J = 12.7 Hz by irr at 4.22), 2.35–3.22 (m, 2 H), 3.73 (s, 3 H), 4.23 (m, 1 H, coalescing to d, J = 8.8 Hz by irr at 2.26), 4.38 (m, 1 H, coalescing to d, J = 8.8 Hz by irr at 2.26); ^{13}C NMR ($CDCl_3$) δ 11.3, 22.3, 25.6, 40.7, 46.7, 51.1, 66.0, 173.6, 176.6. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.15; H, 7.82.

***erythro*-2-[1-(Methoxycarbonyl)propyl]-γ-butyrolactone (2i)**: bp 150 °C (0.6 mmHg); IR (film) 1765 (s), 1730 (s), 1665 (s), 1125 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.1 Hz, 3 H, coalescing to s by irr at 1.86), 1.86 (m, 2 H), 2.31 (m, 2 H), 2.59–3.03 (m, 2 H), 3.69 (s, 3 H), 4.23 (m, 1 H, coalescing to d, J = 8.8 Hz by irr at 2.31), 4.39 (m, 1 H, coalescing to d, J = 8.8 Hz by irr at 2.31); ^{13}C NMR ($CDCl_3$) δ 11.6, 23.2, 25.3, 40.2, 46.5, 51.4, 66.1, 173.5, 177.4; HRMS calcd for $C_9H_{14}O_4$ 186.0892, found m/z (relative intensity) 186.0878 (M, 0.3), 155 (20), 101 (81), 86 (100), 69 (40), 55 (38).

2-[2-(Methoxycarbonyl)propyl]-γ-butyrolactone (3i): a mixture of diastereomers (2/1); bp 150 °C (0.5 mmHg); IR (film) 1765 (s), 1730 (s), 1160 (s), 1125 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, J = 6.8 Hz, one isomer), 1.23 (d, J = 6.8 Hz, 3 H, coalescing to s by irr at 2.70, the other isomer), 1.39–2.06 (m, 3 H), 2.09–2.94 (m, 3 H), 3.69 (s, 3 H), 4.25 (m, 1 H, coalescing to d, J = 9.0 Hz by irr at 2.45), 4.43 (m, 1 H, coalescing to d, J = 9.0 Hz by irr at 2.45); ^{13}C NMR ($CDCl_3$) δ 17.1, 29.0, 34.4, 37.2, 37.6, 51.4, 66.1, 175.7, 178.2 (major isomer); 17.2, 29.1, 34.5, 37.4, 40.2, 51.4, 66.1, 176.0, 178.4 (minor isomer); MS (relative intensity) 186 (M, 0.1), 154 (100), 99 (96), 88 (68), 86 (94), 55 (54). Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.78; H, 7.82.

General Procedure for Palladium(II)-Catalyzed Dicarbonylation and Methoxycarbonylation of 3-Butyn-1-ols (4). A flask equipped as described above for the general preparation of **2** was charged with $PdCl_2$ (17.6 mg, 0.1 mmol) and $CuCl_2$ (404 mg, 3 mmol) and was purged with carbon monoxide. Methanol (9 mL), ethyl orthoacetate (65 mg, 0.4 mmol), propylene oxide (290 mg, 5 mmol), and **4** (1 mmol) were introduced into the flask via a syringe successively in this order, and the mixture was stirred at ambient temperature for the period of time indicated in Tables III and IV. After evaporation of the solvent, ethyl acetate was added and the mixture was filtered with suction through a Celite pad on a funnel. The filter cake was washed several times with ethyl acetate, and the combined filtrates were washed with saturated aqueous $NaHCO_3$. After drying ($MgSO_4$) and evaporation of the solvent, the residue was directly subjected to Kugelrohr distillation under reduced pressure. By this single distillation, spectroscopically pure sample was obtained. For elemental analysis, **5** was purified by column chromatography over silica gel and redistilled, while **6** was purified by column chromatography over basic alumina (activity grade III) since **6** decomposed over silica gel.

(*E*)-2-[(Methoxycarbonyl)(trimethylsilyl)methylidene]-γ-butyrolactone (5a): bp 150 °C (0.2 mmHg); IR (film) 1760 (s), 1720 (s), 1640 (w), 1230 (s), 850 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 2.98 (t, J = 7.3 Hz, 2 H), 3.81 (s, 3 H), 4.39 (t, J = 7.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −2.3 (TMS), 27.2, 51.4, 64.8, 134.6, 146.4, 167.2, 170.2; HRMS calcd for $C_{10}H_{16}O_4Si$ − Me 213.0583, found m/z (relative intensity) 228 (M, 0.9), 213.0560 (M − Me, 91), 197 (33), 181 (37), 169 (56), 89 (100), 73 (29).

(*E*)-2-[(Methoxycarbonyl)(trimethylsilyl)methylidene]-4-methyl-γ-butyrolactone (5b): bp 160 °C (0.2 mmHg); IR (film) 1765 (s), 1725 (s), 1640 (w), 1230 (s), 850 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 1.43 (d, J = 6.1 Hz, 3 H), 2.52 (dd, J = 17.1, 6.3 Hz, 1 H), 3.09 (dd, J = 17.1, 7.3 Hz, 1 H), 3.80 (s, 3 H), 4.65 (sextet, J = 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.3 (TMS), 21.7, 35.1, 51.4, 73.4, 135.9, 146.2, 166.9, 170.2; HRMS calcd for $C_{11}H_{18}O_4Si$ − Me 227.0740, found m/z (relative intensity) 242 (M, 0.2), 227.0735 (M − Me, 23), 213 (16), 183 (20), 169 (11), 123 (12), 89 (59), 73 (28), 61 (23), 43 (100).

(*E*)-2-(1-Methoxyethylidene)-γ-butyrolactone (6c): bp 110 °C (8 mmHg); IR (film) 1705 (s), 1650 (s), 1235 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (t, J = 1.5 Hz, 3 H), 2.87 (tq, J = 9.8, 1.5 Hz, 2 H), 3.71 (s, 3 H), 4.40 (t, J = 9.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 29.8, 50.4, 70.2, 101.9, 166.3, 168.6; HRMS calcd for $C_7H_{10}O_3$ 142.0630, found m/z (relative intensity) 142.0642 (M, 97), 111 (100), 82 (58), 69 (35), 43 (63).

(*E*)-2-(1-Methoxypropylidene)-γ-butyrolactone (6d): bp 120 °C (10 mmHg); IR (film) 1705 (s), 1645 (s), 1260 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (t, J = 7.6 Hz, 3 H), 2.65 (q, J = 7.6 Hz, 2 H), 2.87 (t, J = 9.8 Hz, 2 H), 3.71 (s, 3 H), 4.40 (t, J = 9.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.7, 21.0, 29.8, 50.2, 70.1, 100.7, 166.0, 173.2; HRMS calcd for $C_8H_{12}O_3$ 156.0786, found m/z (relative intensity) 156.0784 (M, 94), 125 (100), 96 (33), 81 (27), 57 (63), 43 (41).

(*E*)-2-(1-Methoxypropylidene)-4-methyl-γ-butyrolactone (6e):[13] bp 120 °C (7 mmHg); IR (film) 1710 (s), 1640 (s), 1255 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (t, J = 7.6 Hz, 3 H), 1.34 (d, J = 6.3 Hz, 3 H), 2.46 (dd, J = 14.2, 7.3 Hz, 1 H), 2.64 (q, J = 7.6 Hz, 2 H), 3.01 (dd, J = 14.2, 9.8 Hz, 1 H), 3.69 (s, 3 H), 4.75 (m, 1 H, coalescing to dd, J = 9.8, 7.3 Hz by irr at 1.34); ^{13}C NMR ($CDCl_3$) δ 11.0, 21.2, 21.6, 36.9, 50.5, 78.5, 99.9, 166.4, 172.5; HRMS calcd for $C_9H_{14}O_3$ 170.0942, found m/z (relative intensity) 170.0933 (M, 51), 153 (66), 139 (64), 109 (83), 69 (70), 58 (100).

(*E*)-2-(1-Methoxy-2,2-dimethylpropylidene)-4-methyl-γ-butyrolactone (6f): bp 130 °C (10 mmHg); IR (film) 1710 (s), 1600 (s), 1250 (s), 1110 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 1.31 (d, J = 6.3 Hz, 3 H), 2.50 (dd, J = 14.2, 7.6 Hz, 1 H), 3.04 (dd, J = 14.2, 10.0 Hz, 1 H), 3.67 (s, 3 H), 4.67 (m, 1 H; coalescing to dd, J = 10.0, 7.6 Hz by irr at 1.31); ^{13}C NMR ($CDCl_3$) δ 21.4, 27.4, (3 C), 34.2, 38.8, 50.3, 77.1, 98.6, 165.7, 176.8; HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found m/z (relative intensity) 198.1253

(M, 100), 167 (63), 156 (54), 139 (87), 109 (60), 57 (91).

(*E*)-2-(1-Methoxy-1-phenylmethylidene)-4-methyl-γ-butyrolactone (6g): bp 140 °C (0.2 mmHg); IR (film) 1715 (s), 1695 (sh), 1630 (m), 1255 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (d, J = 6.1 Hz, 3 H), 2.71 (dd, J = 14.9, 7.8 Hz, 1 H), 3.23 (dd, J = 14.9, 10.0 Hz, 1 H), 3.66 (s, 3 H), 4.92 (m, 1 H, coalescing to dd, J = 10.0, 7.8 Hz by irr at 1.46), 7.10-7.84 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 38.5, 50.6, 78.1, 127.4 (2 C), 129.1 (2 C), 130.0, 130.2, 164.8, 165.6; HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found m/z (relative intensity) 218.0935 (M, 27), 185 (72), 105 (100), 77 (66), 59 (53).

(*Z*)-2-(1-(Methoxycarbonyl)ethylidene)-γ-butyrolactone (7). This sample was prepared according to the similar procedure described for **4**, where an equimolar amount of $PdCl_2$ (194 mg, 1.1 mmol) was used in the absence of $CuCl_2$: IR (film) 1755 (s), 1730 (s), 1675 (s), 1150 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (t, J = 2.0 Hz, 3 H), 2.92 (tq, J = 7.3, 2.0 Hz, 2 H), 3.85 (s, 3 H), 4.40 (t, J = 7.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.9, 25.5, 51.8, 64.9, 124.1, 138.8, 167.8, 168.9; HRMS calcd for $C_8H_{10}O_4$ 170.0579, found m/z (relative intensity) 170.0587 (M, 15), 139 (100), 112 (11), 85 (27), 83 (42), 67 (10), 43 (17).

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Registry No. **1a**, 1123-34-8; **1b**, 624-97-5; **1c**, 60340-28-5; **1d**, 625-31-0; **1e**, 627-27-0; **1f**, 764-37-4; **1g**, 764-38-5; **1h**, 928-97-2; **1i**, 928-96-1; **2a**, 58849-07-3; **2b**, 50598-38-4; *cis*-**2c**, 131067-05-5; *trans*-**2c**, 131067-20-4; *cis*-**2d**, 131067-06-6; *trans*-**2d**, 131067-21-5; **2e**, 19406-00-9; **2f**, 131067-07-7; **2g**, 131067-08-8; **2h**, 131067-09-9; **2i**, 131067-10-2; **3i** (isomer 1), 131067-11-3; **3i** (isomer 2), 131067-12-4; **4a**, 2117-12-6; **4b**, 2117-13-7; **4c**, 10229-10-4; **4d**, 1002-28-4; **4e**, 19781-81-8; **4f**, 131067-13-5; **4g**, 16330-23-7; **5a**, 131078-78-9; **5b**, 131067-18-0; **6c**, 101948-68-9; **6d**, 131067-14-6; **6e**, 131067-15-7; **6f**, 131067-16-8; **6g**, 131067-17-9; **7**, 131067-19-1; acetone, 67-64-1; allylmagnesium bromide, 1730-25-2; cyclohexanone, 108-94-1; dihydrocinnamaldehyde, 104-53-0; 3,3-dimethyl-1-butyne, 917-92-0; 3-pentyn-1-ol, 10229-10-4; propylene oxide, 75-56-9; 1-(1-propenyl)cyclohexanol, 6244-44-6.

Supplementary Material Available: ^{13}C NMR spectra for **2c**, **2i**, **6d-g**, and **7** and ^1H NMR spectra for **5a**, **5b**, and **6c** (10 pages). Ordering information is given on any current masthead page.

Photochemical and Acid-Catalyzed Dienone-Phenol Rearrangements. The Effect of Substituents on the Regioselectivity of 1,4-Sigmatropic Rearrangements of the Type A Intermediate

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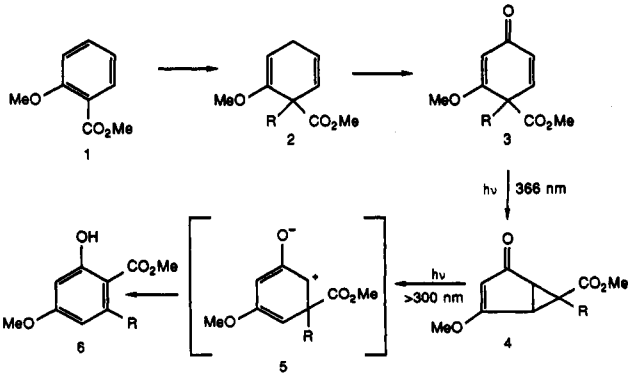
Birch reduction of isophthalic acid and 3-cyanobenzoic acid followed by (1) methylation of the resulting enolate with methyl iodide and (2) esterification with diazomethane provided 2-carbomethoxy- and 2-cyano-6-methyl-6-carbomethoxy-1,4-cyclohexadienes **9** and **25**. Type A photorearrangements of a series of 2-carbomethoxy-, 2-cyano-, 2-methoxy-, and 2-methyl-4-carbomethoxy-4-methyl-2,5-cyclohexadien-1-ones **11**, **26**, **45a**, and **45b** gave 4-carbomethoxy-3-methyl-2-substituted-phenols **12**, **28**, **46**, and **31**. It has been demonstrated that the regioselectivity of type A photorearrangement of C(2) substituted 2,5-cyclohexadien-1-ones is governed by electronic rather than steric effects to give the intermediate C(1) rather than C(3) substituted bicyclo[3.1.0^{1,5}]hex-3-en-2-ones. Regioselectivities of the acid-catalyzed dienone-phenol rearrangements of C(2) substituted 2,5-cyclohexadienones **11**,**45a**, and **45b** appear to be dependent upon the relative stabilities of carbocations resulting from migration of the C(4) carbomethoxy group.

Photorearrangements of 2,5-cyclohexadien-1-ones have attracted the attention of chemists for over 150 years. Outstanding efforts by Zimmerman, Schuster, and many other workers during the last three decades have provided detailed mechanistic understanding of the type A photorearrangement of 2,5-cyclohexadien-1-ones; much of this work already has been reviewed in earlier contributions from this laboratory directed at synthetic aspects of 2,5-cyclohexadien-1-one photochemistry.[1,2]

The type A photorearrangements of 3-methoxy-2,5-cyclohexadien-1-ones **3** give bicyclo[3.1.0]hexenones **4** in excellent yield (Scheme I).[1] While relatively resistant to secondary photorearrangement at 366 nm, bicyclohexenones **4** undergo cyclopropane ring opening when irradiated with light of >300 nm to give zwitterions **5**,[2] from which regioselective 1,2-migrations of the carbomethoxy group give phenols **6**. Cyclohexadienones **3** with a wide variety of alkyl substituents at C(4) are available by alkali metal in ammonia reduction-alkylations[3] of methyl 2-

Scheme I



(1) (a) Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991. (b) Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. *Ibid.* **1988**, *110*, 5547. (c) Schultz, A. G.; Taveras, A. G.; Harrington, R. E. *Tetrahedron Lett.* **1988**, *29*, 3907.

(2) (a) Schultz, A. G.; Macielag, M.; Plummer, M. *J. Org. Chem.* **1988**, *53*, 391. (b) Schultz, A. G. *Pure Appl. Chem.* **1988**, *60*, 981. (c) Schultz, A. G.; Plummer, M. *J. Org. Chem.* **1989**, *54*, 2112.

0022-3263/91/1956-1105$02.50/0