Palladium-Catalyzed Synthesis of 2,3-Dihydro-2-ylidene-1,4-benzodioxins

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Palladium-catalyzed condensation of benzene-1,2-diol with various propargylic carbonates afforded regio- and stereoselectively 2,3-dihydro-2-ylidene-1,4-benzodioxins. The reaction is suggested to proceed by the formation of a (σ-allenyl)palladium complex, followed by the intermolecular attack of the phenoxide ion on this complex to generate a new (σ-allyl)palladium complex in equilibrium with the corresponding (η^3-allyl)palladium complex. Intramolecular attack of the phenoxide ion afforded the corresponding benzodioxan compound. This last attack occurs predominantly at the more electrophilic end of the (η^3-allyl)palladium intermediate. The *Z*- or *E*-stereochemistry of the products was established by ^{1}H NMR and proton NOE measurements and also by X-ray analysis on an example. The *Z*-stereochemistry generally observed is in agreement with the formation of this (η^3-allyl)palladium intermediate. However, in the case of tertiary propargylic carbonates, the *E*-stereochemistry generally observed could be explained by an intramolecular attack of the phenoxide ion on the intermediate (σ-allyl)palladium complex, in slow equilibrium with the (η^3-allyl)palladium complex.

Introduction

Compounds containing 1,4-benzodioxin and 1,4-benzodioxan structures have attracted considerable interest in recent years, mainly due to their interesting biological activities. For example, various 2-substituted 1,4-benzodioxans have shown interesting properties as α- or β-blocking agents and could be used in antidepression or antihypertension therapy.[1] Others exhibit antihyperglycemic properties[2] or act as inhibitors of 5-lipoxygenase.[3] Moreover, the 1,4-benzodioxan structure is found in a variety of biological active natural products.[4] Finally, these compounds could also be used as intermediates for very useful synthetic transformations.[5]

While there are many approaches for the synthesis of 1,4-benzodioxins,[6] the synthetic routes to 2-alkylidene-2,3-dihydro-1,4-benzodioxins are less common. 2-Alkylidene-1,4-dihydro-3-substituted-1,4-benzodioxins have been obtained from the corresponding 2-hydroxymethyl-1,4-benzodioxin through a zinc salt-mediated Mitsunobu substitution,[7a] by an acid-catalyzed ortho ester Claisen rearrangement or by an Eschenmoser procedure.[7b] Condensation of benzene-1,2-diol and methyl 4-chlorobutynoate in acetone in the presence of potassium carbonate afforded a mixture of 1,4-benzodioxinic products.[7c] Pyrocatechol monoprop-2-ynyl ether and analogues were cyclized to the corresponding 2,3-dihydro-2-methylene-1,4-benzodioxins in DMF in the presence of mercuric oxide[7d] or $PdCl_2(PPh_3)_2$[7e] as the catalyst. Monoprop-2-ynylated catechol and 2-hydroxy-3-(prop-2-yloxy)naphthalene reacted with aryl halides in the presence of $PdCl_2(PPh_3)_2$ and CuI in triethylamine to give regio- and stereoselectively the corresponding 2,3-dihydro-2-ylidene-1,4-benzo- and naphthodioxins in good yields.[7f,g] Treatment of 2,3-dibromo-1-propene with the disodium salt of

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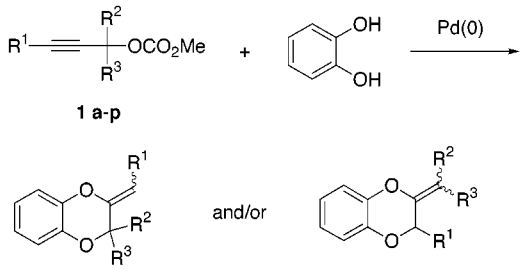
Scheme 1



a $R^1 = R^2 = R^3 = H$
b $R^1 = CH_3$, $R^2 = R^3 = H$
c $R^1 = C_2H_5$, $R^2 = R^3 = H$
d $R^1 = CH_2OTBDMS$, $R^2 = R^3 = H$
e $R^1 = CMe_3$, $R^2 = R^3 = H$
f $R^1 = R^3 = H$, $R^2 = CH_3$
g $R^1 = R^3 = H$, $R^2 = n\text{-}C_5H_{11}$
h $R^1 = R^3 = H$, $R^2 = CH_2Ph$
i $R^1 = R^3 = H$, $R^2 = Ph$
j $R^1 = R^2 = CH_3$, $R^3 = H$
k $R^1 = R^2 = Ph$, $R^3 = H$
l $R^1 = R^2 = CMe_3$, $R^3 = H$
m $R^1 = n\text{-}C_5H_{11}$, $R^2 = Ph$, $R^3 = H$
n $R^1 = CF_3$, $R^2 = n\text{-}C_6H_{13}$, $R^3 = H$
o $R^1 = H$, $R^2 = R^3 = CH_3$
p $R^1 = H$, $R^2 = CH_3$, $R^3 = C_2H_5$
q $R^1 = H$, $R^2 = CH_3$, $R^3 = CH(CH_3)_2$
r $R^1 = H$, $R^2 = CH_3$, $R^3 = PhCH_2$
s $R^1 = R^2 = R^3 = CH_3$
t $R^1 = Ph$, $R^2 = R^3 = CH_3$

catechol in the presence of $Pd(PPh_3)_4$ afforded 2,3-dihydro-2-methylene-1,4-benzodioxin in 67% yield.[7h]

Recently, Tsuji et al. have shown that propargylic carbonates reacted with soft carbon nucleophiles and oxo nucleophiles.[8] The formation of furans was observed using soft carbon nucleophiles such as alkyl acetoacetate or acetylacetone via a double alkylation process, with the alkyl acetoacetate or the acetylacetone behaving as a bisnucleophile.[9] As part of our ongoing interest in developing methods for the preparation of benzodioxan derivatives via organometallic catalysis,[6i,j] we expected that benzene-1,2-diol could react as a bisnucleophile with propargyl carbonates under palladium catalysis to give the expected 2-alkylidene-2,3-dihydro-1,4-benzodioxins according to Scheme 1. We described previously some preliminary results concerning this heteroannulation reaction,[10] and we wish to report in greater detail the results of our investigation, as well as the scope and limitations of this methodology.

Results and Discussion

The conditions described previously for the heteroannulation of benzene-1,2-diol using the bis(carbonate) of 2-buten-1,4-diol were used as our standard reaction conditions [1 equiv of benzene-1,2-diol, 1.2 equiv of propargylic carbonate, 2.5 mol % $Pd_2(dba)_3$, 10 mol % dppb or 1,4-bis(diphenylphosphino)butane, THF, room temperature]. A wide variety of propargylic carbonates were used successfully in this cyclization reaction (Table 1).

Propargyl carbonate **1a** underwent annulation to give 2,3-dihydro-2-methylene-1,4-benzodioxin (**2**) in 81% yield (Table 1, entry 1). The methyl-substituted alkynyl carbonate **1b** gave the corresponding 2,3-dihydro-3-methyl-2-methylene-1,4-benzodioxin (**3**) in 95% yield (Table 1, entry 2). However, substitution of the methyl group by an ethyl, a *tert*-butyldimethylsilyloxymethyl, or a *tert*-butyl group gave a mixture of the two annulated regioisomers, in lower yield in the latter case: carbonate **1c** afforded a 90/10 mixture of compounds **4** and **5**, and carbonates **1d,e** gave compounds **6**/**7** and **8**/**9** in a 31/69, and 25/75 ratio, respectively (Table 1, entries 4 and 5). It is to be noticed that the cyclization leading to benzodioxans **5** and **9** was totally stereoselective, only the *Z*-isomer being obtained, whereas a 90/10 mixture of *Z*/*E*-isomers was obtained in the case of compound **7**.

We then turned our attention to the cyclization reaction using unsubstituted secondary carbonates **1f**−**i**. As expected, carbonate **1f** led to the totally regioselective formation of 2,3-dihydro-3-methyl-2-methylene-1,4-benzodioxin (**3**) (Table 1, entry 6), while carbonates **1g**−**i** gave a mixture of 2,3-dihydro-3-alkyl-2-methylene- and 2,3-dihydro-2-alkylidene-1,4-benzodioxins, the former being predominant (Table 1, entries 7−9). However increasing the steric bulk of the R^2 group favored the cyclization to the alkylidene product, the formation of this compound being highly stereoselective.

Substituted secondary carbonates **1j,k**, having two identical substituents, gave 2,3-dihydro-2-ylidene-1,4-benzodioxins **16** and **17** in quite good yields and with total stereoselectivity, only the *Z*-isomer being formed (Table 1, entries 10 and 11). However no cyclization product was observed using carbonate **1l** bearing two very bulky substituents (Table 1, entry 12).

Propargylic carbonate **1m**, having an *n*-pentyl and a phenyl group as substituents, afforded a mixture of the two regioisomers **18** and **19** (Table 1, entry 13), while the propargylic carbonate **1n**, bearing an *n*-hexyl and a trifluoromethyl group, cyclized regio- and stereospecifically to 2,3-dihydro-2-*n*-hexyl-3-trifluoroethylidene-1,4-benzodioxin (**20**) (Table 1, entry 14).

Condensation of propargylic tertiary carbonates **1o,p** with benzene-1,2-diol afforded regiospecifically the corresponding 2,3-dihydro-3-alkylidene-1,4-benzodioxins **21** and **22** (Table 1, entries 15 and 16). Carbonates **1q,r**, bearing a methyl and an isopropyl group and a methyl and a benzyl group, respectively, afforded a mixture of two regioisomers **23**/**24** and **25**/**26** in a 66/34 and 32/68 ratio, respectively (Table 1, entries 17 and 18); for compounds **24** and **26**, the major stereoisomer had the *E*-stereochemistry. Finally, reaction of benzene-1,2-diol with substituted tertiary carbonates **1s,t** led regio- and stereoselectively to the formation of heterocycles **27** and **28**, having the *Z*-stereochemistry (Table 1, entries 19 and 20).

Since the condensation of carbonate **1d** and benzene-1,2-diol gave a mixture of two functionalized regioisomers **6** and **7** in a 31/69 ratio, we expected that modification of the structure of the palladium catalyst could change this ratio and afford regioselectively one of the regioisomers. Table 2 summarizes the results obtained by modifying the ligand. Among the diphosphines used, the

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(9) (a) Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. (b) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225.
(10) Labrosse, J.-R.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **1999**, *40*, 9025.

Table 1. Reaction of Propargylic Carbonates 1a−t with Benzene-1,2-diol in the Presence of Palladium Catalyst[a]

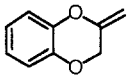
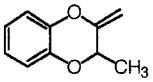
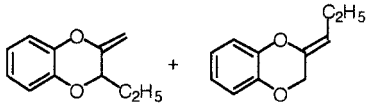
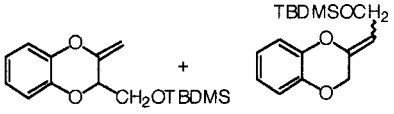
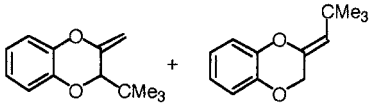
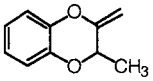
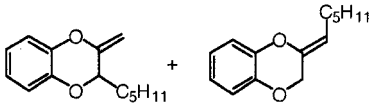
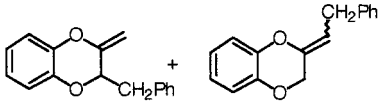
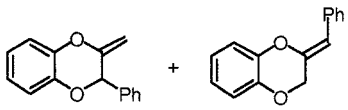
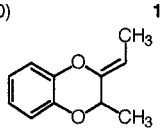
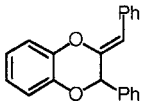
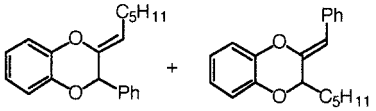
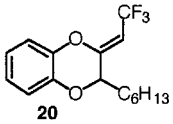
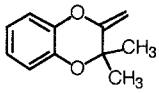
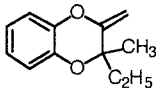
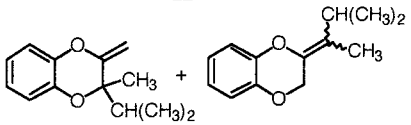
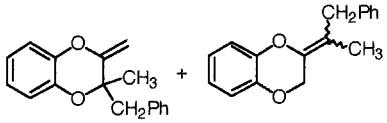
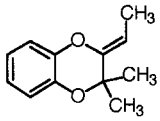
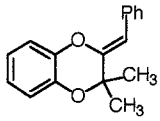
Entry	Carbonate **1**	R^1	R^2	R^3	Products (ratio)[b]	Yields[c] (%)
1	**1a**	H	H	H	 **2**	81
2	**1b**	CH_3	H	H	 **3**	95[e]
3	**1c**	C_2H_5	H	H	 **4** (90) + **5** (10)	97
4	**1d**	$CH_2OTBDMS$	H	H	 **6** (31) + **7** (69) (90:10 *Z*/*E*)	97
5	**1e**	CMe_3	H	H	 **8** (25) + **9** (75)	47
6	**1f**	H	CH_3	H	 **3**	95[e]
7	**1g**	H	n-C_5H_{11}	H	 **10** (87) + **11** (13)	99
8	**1h**	H	$PhCH_2$	H	 **12** (52) + **13** (48) (88:12 *Z*/*E*)	92
9	**1i**	H	Ph	H	 **14** (60) + **15** (40)	92
10	**1j**	CH_3	CH_3	H	 **16**	97
11	**1k**	Ph	Ph	H	 **17**	97
12	**1l**	CMe_3	CMe_3	H	no reaction	-
13	**1m**	n-C_5H_{11}	Ph	H	 **18** (22) + **19** (78)	98
14	**1n**	CF_3	n-C_6H_{13}	H	 **20**	95

Table 1 (Continued)

Entry	Carbonate **1**	R^1	R^2	R^3	Products (ratio)[b]	Yields[c] (%)
15	**1o**	H	CH_3	CH_3	 **21**	90
16	**1p**	H	CH_3	C_2H_5	 **22**	91
17	**1q**	H	CH_3	$CHMe_2$	 **23** (66) + **24** (34) (20:80 *Z*/*E*)	61
18	**1r**	H	CH_3	$PhCH_2$	 **25** (32) + **26** (68) (30:70 *Z*/*E*)	87
19	**1s**	CH_3	CH_3	CH_3	 **27**	55
20	**1t**	Ph	CH_3	CH_3	 **28**	70

[a] Reactions were carried out at room teperature for 24 h using the following ratios: [**1**]:[benzene-1,2-diol]:[$Pd_2(dba)_3$]:[dppb] = 48:40:1:4. [b] Yields refer to chromatographically isolated pure products. [c] Determined by GC and ^1H NMR. [e] Less than 4% of another product, probably 2,3-dihydro-2-propylidene-1,4-benzodioxin, was also formed.

Table 2. Reaction of Propargylic Carbonates 1d with Benzene-1,2-diol in the Presence of Palladium Catalyst[a]

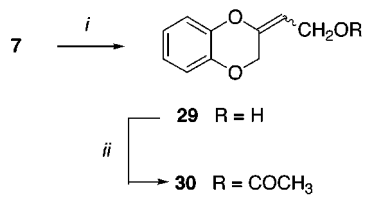
		products		
entry	phosphine	**6** (%)	**7** (%) (*Z*/*E* ratio)	yield (%)
1	dppe	41	59 (93/7)	15
2	dppp	22	78 (92/8)	11
3	dppb	31	69 (89/11)	97
4	dpppe	48	52 (88/12)	60
5	dpph	42	58 (93/7)	98
6	dppf	42	58 (85/15)	92
7	PPh_3	52	48 (88/12)	86
8	$P(C_6H_4\text{-}2\text{-}Me)_3$	17	83 (94/6)	88
9	$P(C_6H_4\text{-}4Me)_3$	50	50 (86/14)	89
10	$P(2\text{-furyl})_3$	21	79 (93/7)	74
11	$P(C_6H_4\text{-}2\text{-}OMe)_3$			0

[a] Reactions were carried out at room teperature for 24 h using the following ratios: [**1**]:[benzene-1,2-diol]:[$Pd_2(dba)_3$]:[-PPh_2] = 48:40:1:4. [b] Yields refer to chromatographically isolated pure products. [c] Determined by GC and ^1H NMR.

highest yields were obtained using dppb, dppf [or 1,1′-bis(diphenylphosphino)ferrocene], and dpph [or 1,6-bis-(diphenylphosphino)hexane], 97, 92, and 98% yield, respectively (Table 2, entries 3, 5, and 6), while dpppe [or 1,5-bis(diphenylphosphino)pentane] gave lower yield (60%, Table 1, entry 4). Practically the same selectivity was observed using these ligands. Conversely dppe [or 1,2-bis(diphenylphosphino)ethane] and dppp [or 1,3-bis-(diphenylphosphino)propane] gave very low yields (Table 2, entries 1 and 2). The very large difference between dppe and dppp, on one hand, and dppb, dpppe, dpph, and dppf, on the other hand, could be related to the larger cone angle of the later diphoshines. Monophosphines such as triphenylphosphine, tris(*p*-tolyl)phosphine), tris(*o*-tolyl)phosphine, and tris(furyl)phosphine also gave good yields of cyclized products (Table 2, entries 7−10). However comparison of entries 8−10 showed that the regioselectivity is probably under steric control; $P(C_6H_4\text{-}2\text{-}Me)_3$ having a larger cone angle than PPh_3 and $P(C_6H_4\text{-}4\text{-}Me)_3$ (145 vs 194°, respectively), gave predominantly the regioisomer **7**, although the two former gave a 50/50 mixture of the two regioisomers **6** and **7**. The more basic tris(*o*-methoxyphenyl)phosphine gave no reaction at all.

Identification of Structures. The structure of these heterocyclic compounds could be assigned from ^1H and ^{13}C NMR spectra and elemental analysis. The heteroannulation was found to be highly stereoselective, the *Z*-isomer being exclusively or almost exclusively obtained. This *Z*-stereochemistry was assigned on the basis of several pieces of evidence. For compound **7** for example, the olefinic proton signal of the major isomer appears at higher field (δ 4.91 ppm) than the minor one (δ 5.45 ppm), due to the deshielding effect of the oxygen of the 1,4-benzodioxane ring system. We can therefore attribute the *Z*-configuration to the major isomer according to the litterature references.[11] However, to confirm this attribution, compound **7** was desilylated and then acetylated to

Scheme 2



Reagents: *(i)* $Bu_4NF.3H_2O$, THF (95%); *(ii)* CH_3COCl, C_5H_5N, CH_2Cl_2, 0 °C (99%)

give acetate **30** (Scheme 2). We noticed again that the chemical shift of the vinylic proton in the *E*-isomer was further downfield (δ 5.47 ppm) than the corresponding one in the *Z*-isomer (δ 4.95 ppm). Moreover, this assignment was confirmed by the proton NOE measurement: when the methylene protons of the ring of the major isomer of compound **30** (δ 4.50 ppm) were irradiated, the vinylic proton signal of the major isomer at δ 4.95 ppm showed a strong enhancement (5.8%). This experiment confirmed the *Z*/*E*-stereochemistry of the double bond for compound **7**. For compound **13**, which is also a mixture of two stereoisomers, we observed again for the vinylic proton of the major isomer a signal at higher field (δ 4.95 ppm) than for the minor isomer (δ 5.43 ppm), in agreement with a *Z*-stereochemistry for the major isomer. Moreover, irradiation of the OCH_2 signal of the major isomer at δ 4.47 ppm led to a 7.4% enhancement of the vinylic proton signal at δ 4.95 ppm.

For compounds **5**, **9**, **11**, **16**, **18**, **20**, and **27**, which are obtained as a single stereoisomer, we noticed that the signal of the vinylic proton was at δ 4.55−4.96 ppm, very close to the values observed for the vinylic proton anti to the oxygen ring (δ 4.75 ppm). Moreover, irradiation of the proton α to the oxygen for compounds **9**, **16**, and **20** afforded an enhancement of the signal of the vinylic proton of 5.9, 2.1, and 9.2%, respectively, in agreement with a *Z*-configuration. When the vinylic proton of compound **18** or the methyl group of compound **27** was irradiated, an enhancement of the olefinic proton signal of 6.3 and 2.9%, respectively, was observed, confirming the *Z*-configuration. For compounds **15**, **17**, **19**, and **28**, bearing a phenethylydene substituent, irradiation of the allylic proton of the ring (compounds **15** and **17**), the vinylic proton (compound **19**), or the methyl group (compound **26**) showed an enhancement of respectively the vinylic proton signal (9.8 and 9.0%), the allylic proton signal (11.3%), and the vinylic proton signal (3.9%). These results allowed the unambiguous attribution of the *Z*-stereochemistry for all these compounds.

Concerning compound **24**, irradiation of the signal of the OCH_2 group of the major isomer at δ 4.70 ppm showed an enhancement of 10.9% of the signal of the methyl of the isopropylidene group at δ 1.10 ppm, and conversely irradiation the signal at δ 1.10 ppm showed an enhancement of 17% of the signal of the OCH_2 group. Irradiation of the signal of the methyl group of the same isomer at δ 1.75 showed no enhancement. For heterocycle **26**, an enhancement of 7.7% of the OCH_2 signal of the major isomer was observed by irradiation of the benzylidene signal of the major isomer at δ 4.76 ppm, while no effect was observed by irradiation of the benzylidene signal of the minor isomer at δ 4.68 ppm. Finally, the X-ray diffraction study of 2-benzylidene-2,3-dihydro-3-phenyl-1,4-benzodioxin (**17**) was also performed and confirmed the *Z*-stereochemistry of this compound.

Mechanism. The reaction is believed to proceed according to Scheme 3. Propargylic carbonate **1** reacts with palladium(0) to generate an allenylpalladium intermediate **A** and methanoate anion. Attack of the monoanion of benzene-1,2-diol on the central sp carbon of this intermediate **A** gives a new intermediate **B**. Abstraction of the proton from the secondary hydroxyl function forms a new (σ-allyl)palladium complex which equilibrates to (*syn*- and (*anti*-η^3-allyl)palladium intermediates **D**. Intramolecular nucleophilic displacement by the phenoxide provides the observed products and regenerates the palladium(0) catalyst. According to this mechanism, the regio- and stereoselectivity of this process arises from the (η^3-allyl)palladium displacement step.

Concerning the regioselectivity of the process, carbonates **1b,c,f,g,o**−**q,s,t** led to differently substituted (η^3-allyl)palladium intermediates **D** (monosubstituted, disubstituted on the same end of the π-allyl, or trisubstituted), and we observed that the ring formation by oxygen displacement occurred preferentially, almost exclusively, at the more substituted end of the allylic system (Table 1, entries 2, 3, 6, 7, 15, 16, 19, and 20). Carbonates **1e,h,i,q,r** gave also unsymmetrical η^3-allyl intermediates; however, **1e** led to the formation of the regioisomer **9** only (Table 1, entry 5), arising from the attack on the less hindered end of the η^3-allyl intermediate, while a mixture of regioisomers was obtained in the other cases (Table 1, entries 8, 9, 17 and 18). This regioselectivity could be explained in the following way. The (η^3-allyl)palladium intermediate **D** is a cationic species, with the charge lying preferentially at the more substituted carbon for electronic reasons. Allylic substitution at this more electrophilic carbon gives the observed products. The opposite regioselectivity observed concerning the attack for entry 5, and even for entries 17 and 18, could be attributed to steric hindrance, the more substituted and electrophilic end being now too crowded. This is in agreement with results observed by Larock et al. in the palladium-catalyzed annulation of 1,2-dienes.[12]

Introduction of an electron-withdrawing group such as CF_3 on one termini of the η^3-allyl intermediate affords exclusively regioisomer **20**, resulting from the attack of the nucleophile on the effectively more electrophilic carbon of the η^3-allyl intermediate (Table 1, entry 14). Introduction of a phenyl (Table 1, entries 9 and 13) or a benzyl group (Table 1, entries 8 and 18) on one end of the η^3-allyl system modifies also the relative electrophilicity of the two termini of the η^3-allyl intermediate and affords a mixture of the two regioisomers.

To confirm this hypothesis, we condensed benzene-1,2-diol with carbonates **1m,u,w** and acetates **31a,b**, bearing various substituents on the phenyl ring, in the presence of palladium(0). We assumed that the intermediate η^3-allyl complex with a positive charge on the carbon bearing the aryl group will be destabilized in the case of an electron-withdrawing group and stabilized in the case of an electron-donating group; so the presence of an electron-donating group would increase the amount of

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Scheme 3

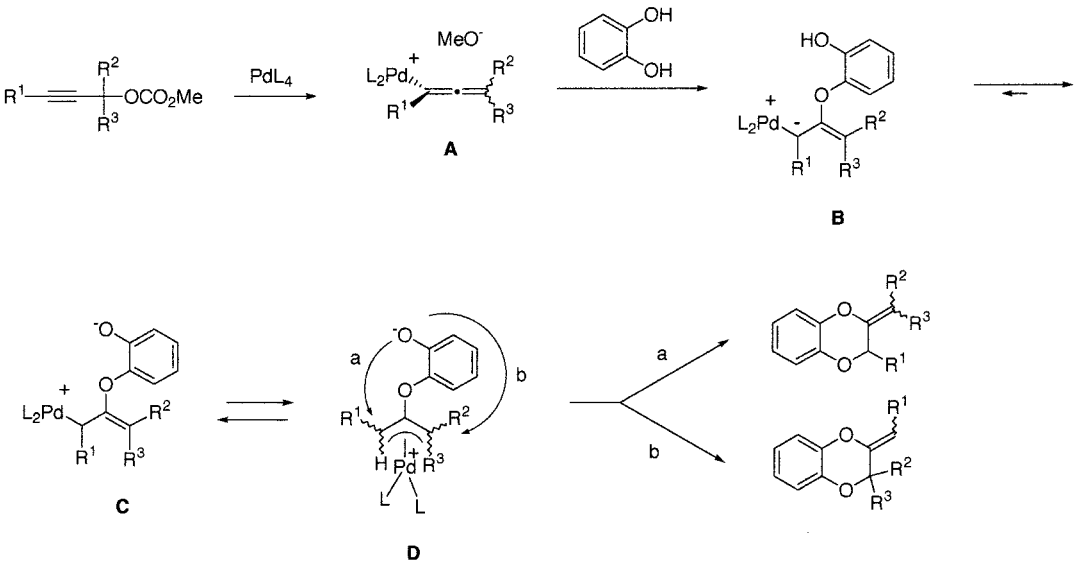
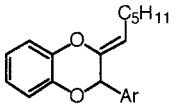
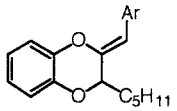


Table 3. Reaction of Propargylic Carbonates 1m,u−w and Acetates 31a,b with Benzene-1,2-diol in the Presence of Palladium Catalyst[a]

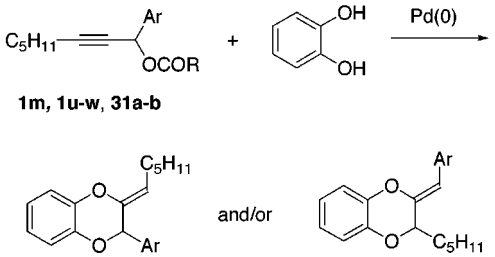
Entry	Substrate	Products (Ratios %)		Yield (%)
				
1	**1m**	**18** (22)	**19** (78)	98
2	**1u**	**32** (25)	**33** (75)	96
3	**1v**	-	**34** (100)	87
4	**1w**	-	**35** (100)	96
5	**31a**	-	**35** (100)	84
6	**31b**	**36** (38)	**37** (62)	88

[a] Reactions were carried out at room teperature for 24 h using the following ratios: [**1** or **31**]:[benzene-1,2-diol]:[$Pd_2(dba)_3$]:[dppb] = 0.48:40:1:4. [b] Yields refer to chromatographically isolated pure products. [c] Determined by GC and ^1H NMR.

2-aryl-2,3-dihydro-3-hexylidene-1,4-benzodioxine, and reversely an electron-withdrawing group would increase the amount of 2-benzylidene-2,3-dihydro-3-pentyl-1,4-benzodioxine. The results summarized in Table 3 are in quite good agreement with this hypothesis. Carbonate **1u** gave a mixture of two regioisomers **32** and **33** (Table 3, entry 2), in a 25/75 ratio, quite closed to that obtained using carbonate **1m**. Carbonate **1w**, or acetate **31a** in the presence of NEt_3, having an electron-withdrawing group, afforded only the cyclized regioisomer **35**. Conversely acetate **31b** bearing an electron-donating group gave the two regioisomers **36** and **37** in a 38/62 ratio. Carbonate **1v** afforded also regiospecifically the cyclized product **34** only, but this is probably due to steric reason. It is to be noticed that NOE experiments showed that all stereoisomers have the *Z*-configuration; for example, irradiation of the signal of the vinylic proton of **36** at δ 4.45−4.60 ppm showed an enhancement of 3.8% of the signal of the benzylic proton at δ 5.40 ppm, although irradiation of the signal of the benzylic proton of **37** at δ 5.55 ppm showed an enhancement of 7.8% of the signal of the vinylic proton at δ 4.45−4.60 ppm.

2,3-Dihydro-2-ylidene-1,4-benzodioxins bearing only one substituent on the double bond had mainly, if not exclusively, the *Z*-stereochemistry. This could be explained on the basis of the π-allyl mechanism (Scheme

Scheme 4

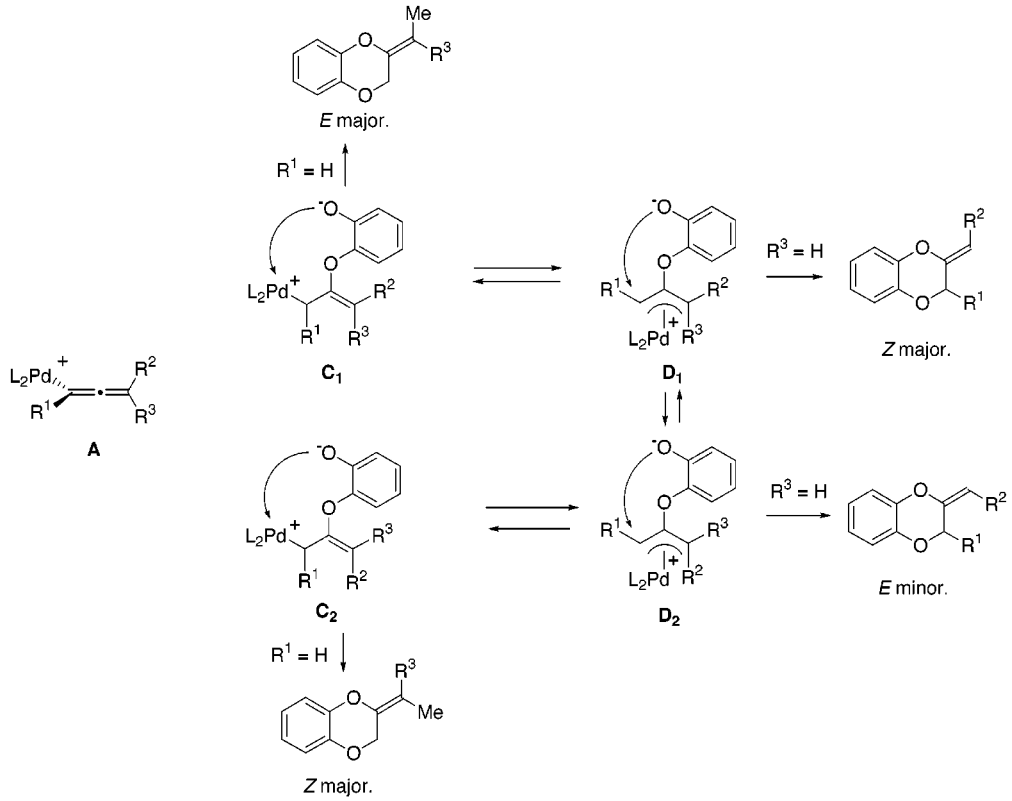


1m, 1u-w, 31a-b

1m Ar = C_6H_5, R = OCH_3
1u Ar = C_6H_4-4-CH_3, R = OCH_3
1v Ar = C_6H_2-tri(2,4,6)-CH_3, R = OCH_3
1w Ar = C_6H_4-4-CN, R = OCH_3
31a Ar = C_6H_4-4-CN, R = CH_3
31b Ar = C_6H_4-4-OCH_3, R = CH_3

5). Effectively attack of the phenoxide on the σ-allenyl complex **A** afforded, after hydrogen exchange, two diastereoisomeric (σ-allyl)palladium complexes $\mathbf{C_1}$ and $\mathbf{C_2}$ that are in equilibrium with the corresponding η^3-allyl complexes $\mathbf{D_1}$ and $\mathbf{D_2}$ (R_3 = H). In this case the stereoselectivity depends on the relative abundance of the different (*syn*- and (*anti*-η^3-allyl)palladium intermediates $\mathbf{D_1}$ and $\mathbf{D_2}$. The controlling factor seems to be the steric hindrance in the (η^3-allyl)palladium intermediates. In the (*anti*-η^3-allyl)palladium complex $\mathbf{D_1}$, the steric hindrance

Scheme 5



is higher than in the (*syn*-η^3-allyl)palladium complex $\mathbf{D_2}$; attack of the phenoxide gives predominantly the *Z*-stereoisomer.

However 2,3-dihydro-2-ylidene-1,4-benzodioxins **24** and **26** bearing two substituents on the double bond exhibited mainly the *E*-stereochemistry. To explain this quite different behavior, we postulated that, due to steric hindrance on the double bond, the $\sigma \rightleftharpoons \eta^3 \rightleftharpoons \sigma$ equilibrium leading to the formation of the (η^3-allyl)pallladium intermediates **D** is slower in these two examples. There is therefore a competition between the attack of the phenoxide on the (η^3-allyl)palladium and on the (σ-allyl)-palladium intermediates. It was shown previously that the attack on the (η^3-allyl)palladium intermediate occurred predominantly, if not entirely, at the more substituted termini of the η^3-allyl system affording in these cases the two compounds **23** and **25**. Comparison of entries 15−18 in Table 1 shows that the substitution of a methyl group by an isopropyl or a benzyl group favors the formation of compounds **24** and **26**. The major *E*-stereochemistry observed for these compounds could be explained by assuming that they are formed mainly by the second attack of the phenoxide on the (σ-allyl)-palladium complexes **C**. Attack of the phenoxide on the (σ-allenyl)palladium complex **A** gives two diastereoisomeric (σ-allyl)palladium complexes $\mathbf{C_1}$ and $\mathbf{C_2}$. We could expected this attack to occur from the less sterically hindered side, affording in this case predominantly the stereoisomer $\mathbf{C_1}$ ($R^2 = CH_3$), which will give the *E*-isomer.

Conclusion

The palladium-catalyzed condensation of benzene-1,2-diol with various propargylic carbonates provides a versatile and easy access to a wide variety of 2,3-dihydro-2-ylidene-1,4-benzodioxins with quite good yields. The process is often quite regio- and stereoselective, the major regioisomer being formed by the intramolecular attack of the phenoxide ion on the more electrophilic termini of the (η^3-allyl)palladium intermediate. The stereochemistry of the double bond in the resulting heterocycle depends on substitution pattern of the propargylic carbonate: primary and secondary carbonates afforded mainly, if not at all, the *Z* alkene, although tertiary carbonates gave predominantly the *E*-isomer.

Experimental Section

Reactions involving palladium catalysis were performed in Schlenk tubes under a nitrogen atmosphere. Solvents and reagents were purified by conventional methods. Thin-layer chromatography was performed on precoated sheets $60F_{254}$, and silica gel chromatography was done using Merck SiO_2 (Gerudan SI 60, 0.040−0.063 mm). Melting points are uncorrected. ^{1}H NMR solutions were recorded at 200 or 300 MHz, and ^{13}C NMR spectra at 75 MHz; NMR chemical shifts are reported in ppm downfield from TMS, and *J* values are given in hertz. $Pd_2(dba)_3$, triphenylphosphine, tris(2-methylphenyl)-phosphine, tris(4-methylphenyl)phosphine, tris(2-furyl)phosphine, tris(2-methoxyphenyl)phosphine, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, 1,5-bis(diphenylphosphino)pentane, 1,6-bis(diphenylphosphino)hexane, and benzene-1,2-diol were purchased from a commercial source.

Alcohols used as starting materials for the synthesis of carbonates **1d**,[13] **1e**,[14] **1h**,[15] **1k**,[16] **1l**,[17] **1m**,[18] **1n**,[19] **1r**,[20] **1s**,[21]

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and **1t**,[22] as well as carbonates **1a**,[23] **1b**,[9b] **1c**,[9b] **1d**,[24] **1g**,[25] **1i**,[26] **1j**,[9b] and **1o**,[9b] were prepared according to known procedures. Dihydrobenzodioxins **2**,[7g] **15**,[7g] and **21**[27] have already been described.

General Procedure for the Palladium-Catalyzed Annulation Reactions. A mixture of $Pd_2(dba)_3$ (20.8 mg, 2.2 × 10^{-2} mmol) and diphosphine (9.1 × 10^{-2} mmol) or monophosphine (18.2 × 10^{-2} mmol), in THF (7 mL), was stirred under a nitrogen atmosphere at room temperature for 30 min. This catalyst solution was added to a mixture of benzene-1,2-diol (100 mg, 0.9 mmol) and the corresponding propargylic carbonate (1.1 mmol) or the corresponding acetate (1.1 mmol) in the presence of triethylamine (267 mg, 2.6 mmol). The resulting solution was stirred at room temperature for 24 h. The solvent was evaporated and the residue chromatographed over silica eluting with petroleum ether/ethyl acetate to afford the corresponding 2,3-dihydro-1,4-benzodioxin. The yields of the products from the reactions are listed in Tables 1−3. The spectral data of some of the compounds are listed below, and others have been incorporated in the Supporting Information.

2,3-Dihydro-2-methyl-3-methylene-1,4-benzodioxin (3): oil; R_f 0.3 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.55 (d, J = 6.6 Hz, 3H, CH_3), 4.41 (d, J = 1.5 Hz, 1H, =CH_2), 4.54 (q, J = 6.6 Hz, 1H, $CHCH_3$), 4.74 (d, J = 1.5 Hz, 1H, =CH_2), 6.80−7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 17.4, 69.2, 89.7, 116.1, 117.3, 122.0, 122.2, 142.5, 143.1, 154.2. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 73.84; H, 6.37.

2,3-Dihydro-2-ethyl-3-methylene-1,4-benzodioxin (4): obtained as an inseparable mixture of the two regioisomers **4** and **5**; oily mixture; R_f 0.54 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.3 Hz, 3H, CH_3), 1.75−1.95 (m, 2H, CH_2), 4.32−4.44 (m, 2H, OCH, =CH_2), 4.78 (d, J = 2.0 Hz, 1H, =CH_2), 6.80−7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 9.9, 24.6, 74.8, 90.7, 116.1, 117.5, 121.9, 122.3, 142.4, 142.5, 152.6. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.96; H, 6.87. Found: C, 74.76; H, 6.92.

***(Z)*-2,3-Dihydro-2-propylidene-1,4-benzodioxin (5):** obtained as an inseparable mixture of the two regioisomers **4** and **5**; oily mixture; R_f 0.8 (petroleum ether/ethyl acetate 10/1); ^{1}H NMR ($CDCl_3$) δ 1.10 (m, 3H, CH_3), 2.25−2.40 (m, 2H, CH_2CH_3), 4.46 (s, 2H, OCH_2), 4.74 (t, J = 7.3 Hz, 1H, =CH), 6.80−7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.5, 65.5, 110.2, 116.6, 117.4, 121.9, 122.1, 143.1, 144.2, 152.6.

***tert*-Butyldimethyl[(2,3-dihydro-3-methylene-1,4-benzodioxin-2-yl)methox y]silane (6):** oil; R_f 0.2 (petroleum ether/ethyl acetate 80/1); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.88 (s, 9H, CH_3), 3.85 (dd, J = 10.9, 5.9 Hz, 1H, CH_2), 3.85 (dd, J = 10.9, 6.3 Hz, 1H, CH_2), 4.45 (d, J = 1.8 H, 1H, =CH_2), 4.56 (dd, J = 6.3, 5.9 Hz, 1H, CHO), 4.80 (d, J = 1.8 H, 1H, =CH_2), 6.80−7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ −5.4, 18.3, 25.8, 62.9, 74.2, 92.2, 116.1, 117.4, 121.9, 122.3, 142.0, 142.1, 150.3. Anal. Calcd for $C_{16}H_{24}O_3Si$: C, 65.72; H, 8.28. Found: C, 65.39; H, 8.61.

***tert*-Butyldimethyl[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane (7):** obtained as an inseparable mixture of the *Z*- and *E*-isomers (*Z*/*E* 90/10); oily mixture; R_f 0.24 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 6H, $SiCH_3$), 0.88 (s, 9H, CH_3), 4.27 (d, J = 7.0 Hz, 0.2H, =$CHCH_2O$), 4.47 (d, J = 6.3 Hz, 1.8H, =$CHCH_2O$), 4.47 (s, 1.8H, OCH_2), 4.69 (s, 0.2H, OCH_2), 4.91 (t, J = 6.3 H, 0.9H, =CH), 5.45 (t, J = 7.0 H, 0.1H, =CH), 6.80−7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ −5.1, 18.4, 26.0 *(E)*, 26.1 *(Z)*, 56.6 *(Z)*, 57.8 *(E)*, 60.6 *(E)*, 65.1 *(Z)*, 107.0 *(E)*, 107.7 *(Z)*, 116.5 *(E)*, 116.6 *(Z)*, 117.2 *(E)*, 117.4 *(Z)*, 122.0 *(E)*, 122.2 *(Z)*, 122.3, 142.6, 143.2, 144.0. Anal. Calcd for $C_{16}H_{24}O_3Si$: C, 65.72; H, 8.28. Found: C, 65.39; H, 8.61.

***(Z)*-2,3-Dihydro-2-ethylidene-3-methyl-1,4-benzodioxin (16):** oil; R_f 0.24 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.50 (d, J = 6.4 Hz, 3H, CH_3), 1.76 (d, J = 7.0 Hz, 3H, CH_3), 4.51 (q, J = 6.4 Hz, 1H, OCH), 4.84 (q, J = 7.0 Hz, 1H, =CH), 6.80−7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 9.4, 17.4, 69.7, 100.7, 116.2, 117.3, 121.8, 121.9, 142.8, 143.2, 147.2. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.96; H, 6.87. Found: C, 74.61; H, 6.68.

***(Z)*-2-Benzylidene-2,3-dihydro-3-phenyl-1,4-benzodioxin (17):** white solid; mp 68−70 °C; R_f 0.52 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 5.45 (s, 1H, OCH), 5.70 (s, 1H, =CH), 7.00−7.80 (m, 14H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 76.7, 109.3, 116.6, 117.9, 122.9, 127.2, 127.9, 128.6, 128.8, 129.3, 134.4, 136.7, 142.5, 143.6, 146.2. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.97; H, 5.37. Found: C, 83.91; H, 5.50.

***(Z)*-2,3-Dihydro-2-n-hexylidene-3-phenyl-1,4-benzodioxin (18):** obtained as an inseparable mixture of the two regioisomers **18** and **19**; oily mixture; R_f 0.36 (petroleum ether/ethyl acetate 10/1); ^{1}H NMR ($CDCl_3$) δ 0.95−1.10 (m, 3H, CH_3), 1.32−1.52 (m, 6H, CH_2), 2.39 (bs, 2H, CH_2), 4.55−4.70 (m, 1H, =CH), 5.68 (s, 1H, OCH), 6.80−7.90 (m, 9H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.6, 24.3, 29.1, 76.1, 110.1, 117.7, 122.1, 122.2, 128.6, 127.8, 137.0, 143.1, 143.6, 145.5. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.61; H, 7.66.

***(Z)*-2-Benzylidene-2,3-dihydro-3-n-pentyl-1,4-benzodioxin (19):** obtained as an inseparable mixture of the two regioisomers **18** and **19**; oily mixture; R_f 0.49 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 0.95−1.10 (m, 3H, CH_3), 1.32−1.52 (m, 6H, CH_2), 1.90 (m, 2H, CH_2), 4.55−4.70 (m, 1H, =CH), 5.56 (s, 1H, OCH), 6.80−7.90 (m, 9H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.7, 25.3, 31.6, 31.7, 75.0, 106.5, 116.4, 117.9, 122.0, 122.9, 127.0, 128.5, 129.1, 133.5, 142.3, 142.4, 146.0.

***(Z)*-2,3-Dihydro-2-n-hexyl-2-(2,2,2-trifluoroethylidene)-1,4-benzodioxin (20):** oil; R_f 0.5 (petroleum ether/ethyl acetate 150/1); ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 6.6 Hz, 3H, CH_3), 1.25−1.90 (m, 10H, CH_2), 4.45 (t, J = 7.5 Hz, 1H, OCH), 4.96 (q, J = 6.8 Hz, 1H, =CH), 6.92−7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 25.0, 28.8, 30.9, 31.6, 73.0, 95.0 (q, J = 35.6 Hz), 116.6, 117.7, 122.5, 123.7, 124.8 (q, J = 269.6 Hz), 141.2, 141.8, 154.1 (q, J = 5.1 Hz); ^{19}F δ −57.7. Anal. Calcd for $C_{16}H_{19}F_3O_2$: C, 63.97; H, 6.38. Found: C, 64.09; H, 6.20.

2,3-Dihydro-2-ethyl-2-methyl-3-methylene-1,4-benzodioxin (22): oil; R_f 0.31 (petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.65−1.75 (m, 2H, CH_2), 4.43 (s, 1H, =CH_2), 4.72 (s, 1H, =CH_2), 6.80−7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 8.1, 22.3, 29.4, 75.6, 90.1, 115.6, 117.5, 121.5, 122.3, 141.6, 142.3, 155.7. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.75; H, 7.65.

2,3-Dihydro-2-isopropyl-2-methyl-3-methylene-1,4-benzodioxin (23): obtained as an inseparable mixture of the two regioisomers **23** and **24**; oily mixture; R_f 0.50 (petroleum ether/ethyl acetate 15/1); ^{1}H NMR ($CDCl_3$) δ 0.92 (d, J = 6.8 Hz, 3H, CH_3), 0.94 (d, J = 6.8 Hz, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.88 (hept, J = 6.8 Hz, 1H, $CHMe_2$), 4.44 (d, J = 1.9 Hz, 1H, =CH_2), 4.80 (d, J = 1.9 Hz, 1H, =CH_2), 6.88 (bs, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 15.8, 17.4, 18.5, 30.3, 78.7, 91.3, 115.8, 117.7, 121.8, 122.6, 141.5, 143.0, 155.5. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.90. Found: C, 76.62; H, 8.02.

2,3-Dihydro-2-(1,2-dimethylbut-1-enylidene)-1,4-benzodioxin (24): obtained as an inseparable mixture of the two regioisomers **23** and **24**; oily mixture; R_f 0.50 (petroleum ether/ethyl acetate 15/1); ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 7.0 Hz, 1.2 H, CH_3 *(Z)*), δ 1.10 (d, J = 6.8 Hz, 4.8 H, CH_3 *(E)*), 1.59 (s, 0.6H, CH_3 *(Z)*), 1.75 (s, 2.4H, CH_3 *(E)*), 2.70 (hept, J = 6.8 Hz, 0.8 H, $CHMe_2$ *(E)*), 3.38 (hept, J = 7.0 Hz, 0.8 H, $CHMe_2$ *(Z)*), 4.60 (s, 0.4 H, CH_2 *(Z)*), 4.70 (s, 1.6 H, CH_2 *(E)*), 6.80−7.00 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 9.0 *(E)*, 10.7 *(Z)*, 20.6 *(Z)*, 21.6

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(E), 26.7 *(Z)*, 29.0 *(E)*, 61.3 *(E)*, 62.0 *(Z)*, 116.8 *(E)*, 117.4 *(E)*, 120.8 *(Z)*, 121.3 *(Z)*, 121.7 *(E)*, 122.2, 136.7 *(Z)*, 137.3 *(E)*, 144.0, 144.3, 144.4.

2-Benzyl-2,3-dihydro-2-methyl-3-methylene-1,4-benzodioxin (25): obtained as an inseparable mixture of the two regioisomers **25** and **26**; oily mixture; R_f 0.36 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3H, CH_3), 2.90 (d, J = 13.6 Hz, 1H, CH_2), 3.05 (d, J = 13.6 Hz, 1H, CH_2), 4.31 (d, J = 2.0 Hz, 1H, =CH_2), 4.74 (d, J = 2.0 Hz, 1H, =CH_2), 6.80−7.35 (m, 9H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 22.6, 42.6, 75.5, 91.3, 115.9−130.7, 139.2, 136.0−144.0, 155.1. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.40. Found: C, 80.86; H, 6.44.

2,3-Dihydro-2-(1-methyl-2-phenylethylidene)-1,4-benzodioxin (26): obtained as an inseparable mixture of the two regioisomers **25** and **26**; oily mixture; R_f 0.45 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 0.9H, CH_3 *(Z)*), 1.72 (s, 2.1H, CH_3 *(E)*), 3.41 (s, 1.4H, OCH_2 *(E)*), 3.62 (s, 0.6H, OCH_2 *(Z)*), 4.68 (s, 0.6H, CH_2 *(Z)*), 4.76 (s, 1.4H, CH_2 *(E)*), 6.80−7.35 (m, 9H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 14.6 *(E)*, 15.6 *(Z)*, 36.4 *(E)*, 37.9 *(Z)*, 61.4, 114.2 *(E)*, 114.3 *(Z)*, 115.9−130.7, 136.0 *(E)*, 138.3 *(Z)*,136.0−144.0, 144.1.

***(Z)*-2,3-Dihydro-2,2-dimethyl-3-ethylidene-1,4-benzodioxin (27):** oil; R_f 0.50 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 6H, CH_3), 1.78 (d, J = 6.8 Hz, 3H, CH_3), 4.92 (q, J = 6.8 Hz, 1H, =CH), 6.75−7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 9.6, 25.2, 73.0, 99.6, 115.8, 117.5, 121.3, 122.0, 141.8, 142.4, 149.6. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 76.05; H, 7.44.

***(Z)*-3-Benzylidene-2,3-dihydro-2,2-dimethyl-1,4-benzodioxin (28):** white solid; mp 54−57 °C; R_f 0.22 (petroleum ether/ethyl acetate 100/1); ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 6H, CH_3), 5.73 (s, 1H, =CH), 6.90−7.00 (m, 3H, H_{arom}), 7.10−7.15 (m, 1H, H_{arom}), 7.23−7.30 (m, 1H, H_{arom}), 7.38 (t, J = 7.3 Hz, 2H, H_{arom}), 7.72 (d, J = 7.3 Hz, 2H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 25.4, 73.5, 104.1, 115.9, 117.7, 121.6, 122.7, 126.9, 129.1, 134.6, 134.6, 141.9, 149.8. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.40. Found: C, 80.82; H, 6.37.

2,3-Dihydro-1,4-benzodioxin-2-ylideneethanol (29). A solution of compound **7** (2.6 g, 9 mmol) and $Bu_4NF{\cdot}3H_2O$ (4.6 g, 18 mmol) in THF (80 mL) was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was diluted with diethyl ether (100 mL), and the etheral solution washed with water (3 × 40 mL). Evaporation of the solvent gave a residue that was purified by column chromatography to give 1.5 g of compound **29** (95% yield), as an inseparable mixture of the *Z*- and *E*-isomers (*Z*/*E* 90/10): R_f 0.45 (petroleum ether/ethyl acetate 4/3); ^{1}H NMR ($CDCl_3$) δ 2.65 (bs, 1H, OH), 4.17 (d, J = 7.7 Hz, 0.2H, =CHCH_2O), 4.38 (d, J = 7.0 Hz, 1.8H, =CHCH_2O), 4.44 (s, 1.8H, OCH_2), 4.64 (s, 0.2H, OCH_2), 4.93 (t, J = 7.0 H, 0.9H, =CH), 5.53 (t, J = 7.7 H, 0.1H, =CH), 6.80−7.10 (m, 4H, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 55.8 *(Z)*, 56.8 *(E)*, 65.0 *(E)*, 65.9 *(Z)*, 106.5 *(E)*, 106.7 *(Z)*, 116.5 *(E)*, 116.6 *(Z)*, 117.2 *(E)*, 117.4 *(Z)*, 122.2 *(E)*, 122.4 *(E* and *Z)*, 122.5 *(Z)*, 142.4, 143.9, 144.5. These data are in agreement with those published in the literature.[7e]

Acetic Acid 2,3-Dihydro-1,4-benzodioxin-2-ylidene Ethyl Ester (30). To a solution of the alcohol **29** (60 mg, 0.34 mmol) and pyridine (107 mg, 1.35 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added acetyl chloride (107.5 mg, 1.35 mmol). After the mixture was stirred for 24 h at room temperature, a saturated aqueous solution of copper sulfate (10 mL) was added, and the mixture was extracted with diethyl ether (3 × 10 mL). Evaporation of the solvent gave an oil that was purified on silica gel eluting with ethyl acetate/petroleum ether (1/4) to give 73.5 mg of the ester **30** (99% yield) as an inseparable mixture of the *Z*- and *E*-isomers (*Z*/*E* 90/10): R_f 0.54; ^{1}H NMR ($CDCl_3$) δ 2.90 (s, 3H, CH_3), 4.50 (s, 1.8H, OCH_2), 4.65 (d, J = 8.4 Hz, 0.2H, =CHCH_2O), 4.73 (s, 0.2H, OCH_2), 4.85 (d, J = 7.1 Hz, 1.8H, =CHCH_2O), 4.95 (t, J = 7.1 H, 0.9H, =CH), 5.47 (t, J = 8.4 H, 0.1H, =CH), 6.80−7.10 (m, 4H, H_{arom}). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.43; H, 5.50. Found: C, 65.95; H, 5.39.

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Supporting Information Available: Experimental procedures for the preparation of the unknown propargylic alcohols, propargylic carbonates **1a**−**n** and **1u**−**w**, and acetates **31a,b** and spectral data listings for these compounds, analytical and spectral data for compounds **8**−**14** and **32**−**37**, and the X-ray diffraction study data for compound **17** with ORTEP diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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