JOC Article

An Efficient Method for the Synthesis of Vinylbromohydrin and Vinylbromoalkoxy Derivatives and Cyclocarbonylation of α-Allenic Alcohols Catalyzed by Palladium Chloride

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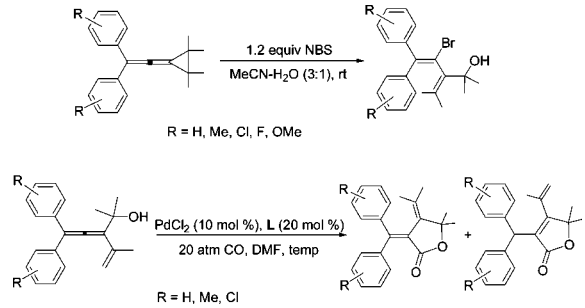

Vinylidenecyclopropanes undergo hydrobromination or alkoxybromination in the presence of *N*-bromosuccinimide and water or alcohols to give the corresponding vinylbromohydrin and vinylbromoalkoxy derivatives in moderate to excellent yields at room temperature. These vinylbromohydrin derivatives can be easily transformed to α-allenic alcohols in the presence of Et_3N under mild conditions. In addition, the cyclocarbonylation of α-allenic alcohols with CO catalyzed by palladium chloride to give the corresponding lactones under different reaction conditions has been described.

Introduction

Hydrobromination of olefinic compounds is a powerful method in organic synthesis to introduce two different functional groups (hydroxy and bromine) into organic molecules by a single step.[1] Thus far, various brominating reagents, such as molecular bromine or *N*-bromosuccinimide (NBS),[2] metal bromide along with an oxidizing agent,[3] and *N*,*N*-dibromo-*p*-toluenesulfonamide ($TsNBr_2$),[4] have been developed to obtain high regio- and stereoselectivity in this reaction.[2−5] However, the hydrobromination of compounds containing highly strained cyclopropane ring moieties has been seldom reported.[6,7] Vinylidenecycloproanes (VDCPs) **1** are one of the most remarkable known organic compounds. They have an allene moiety connected by a cyclopropane ring and yet they are thermally stable and reactive substances in organic synthesis. Much pioneering work has been done for this kind of particular organic compounds involving mechanistic, theoretical, spectroscopic, and synthetic studies as well as thermal and photochemical

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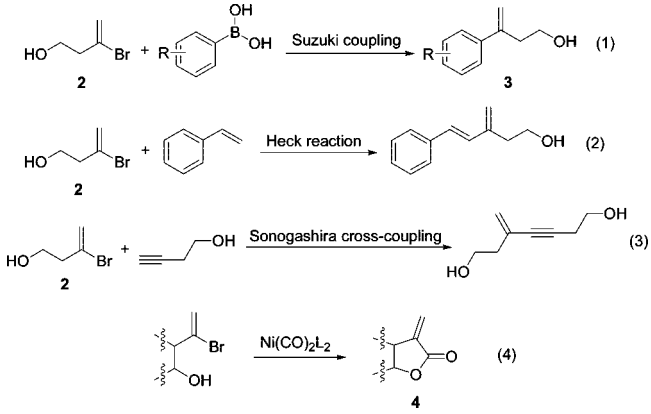
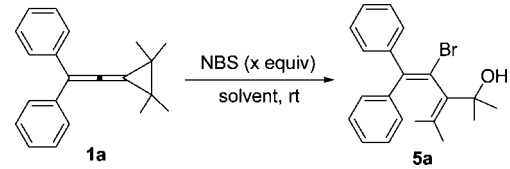
skeletal conversions since the ring-opening of cyclopropanes can gain additional driving force by the relief of angular strain.[8,9]

On the other hand, homoallylic alcohols containing a vinyl bromide moiety, such as compound **2**, are useful building blocks in organic and medicinal chemistry. For example, they could undergo the Suzuki−Miyaura coupling reaction[10] with boronic acids to give the corresponding alcohols **3**, which have been used for the synthesis of *crinane* by Padwa's group (eq 1).[10b] In addition, they could undergo the Heck reaction with alkenes (eq 1)[11] and Sonogashira cross-coupling reactions with alkynes to afford the corresponding coupling products in good yields (eq 1).[12] Moreover, Semmelhack and co-workers have achieved intramolecular carbonylation of **2** to provide methylene lactone **4** by using a nickel carbonyl complex (eq 1).[13]



Although vinylbromohydrins such as compound **2** have wide application in organic synthesis, the synthetic methods to obtain these compounds are still limited.[14] In this paper, we wish to report the hydrobromination of a variety of vinylidenecyclopropanes **1** by NBS and water or alcohols to give the corresponding vinylbromohydrin derivatives **5** or vinylbromoalkoxy derivatives in moderate to excellent yields under mild conditions along with a palladium(II)-catalyzed cyclocarbonylation with carbon monoxide.

TABLE 1. Hydrobromination of Vinylidenecyclopropane 1a by NBS and Water under Various Reaction Conditions



entry[a]	*x*	solvent	time	yield (%)[b] 5a
1	1.2	MeCN−H_2O (4:1)	10 min	84
2	1.2	THF−H_2O (4:1)	2 h	58
3	1.2	acetone−H_2O (4:1)	2 h	69
4	1.2	DMSO−H_2O (4:1)	2 h	trace
5	1.2	DMF−H_2O (4:1)	2 h	55
6	1.2	hexane−H_2O (4:1)	2 h	54
7	1.2	toluene−H_2O (4:1)	2 h	27
8	1.2	CH_2Cl_2−H_2O (4:1)	2 h	66
9	1.2	DCE−H_2O (4:1)	2 h	58
10	1.2	MeCN−H_2O (8:1)	10 min	81
11	1.2	MeCN−H_2O (3:1)	10 min	90
12	1.0	MeCN−H_2O (3:1)	10 min	65
13	1.5	MeCN−H_2O (3:1)	10 min	90

[a] Reaction conditions: VDCP (0.18 mmol), solvent (2 mL), NBS (*x* equiv), rt. [b] Isolated yields.

Results and Discussion

Initial examination was performed by using vinylidenecyclopropane **1a** as the substrate to react with NBS and water in various solvents to develop the optimal conditions and the results of these experiments are summarized in Table 1. We found that the corresponding vinylbromohydrin compound **5a** was produced under various conditions in moderate to high yields. For example, using 1.2 equiv of NBS in MeCN/H_2O (4:1, 8:1 and 3:1) at room temperature (20 °C), the reaction proceeded smoothly to give **5a** in 84%, 81%, and 90% yields within 10 min, respectively (Table 1, entries 1, 10, and 11). However, the reaction became sluggish to produce **5a** in lower yields in many other solvents even after extending the reaction time to 2 h (Table 1, entries 2−9). When using 1.0 and 1.5 equiv of NBS as the brominating reagent in MeCN/H_2O (3:1) at room temperature (20 °C), the reaction proceeded smoothly to give **5a** in 65% and 90% yields within 10 min, respectively (Table 1, entries 12 and 13). These results indicated that the best reaction conditions for this transformation are to carry out the reaction in MeCN/H_2O (3:1) at room temperature in the presence of 1.2 equiv of NBS.

With these optimized reaction conditions being identified, we next examined the hydrobromination of a variety of vinylidenecyclopropanes **1** by NBS and water. The results are shown in Table 2. As for symmetrical vinylidenecyclopropanes **1b** and **1c** and unsymmetrical vinylidenecyclopropanes **1f**, **1g**, and **1h** having electron-donating methyl or methoxy groups on the benzene rings, the corresponding vinylbromohydrin derivatives **5b**, **5c**, **5f**, **5g**, and **5h** were obtained in high yields within

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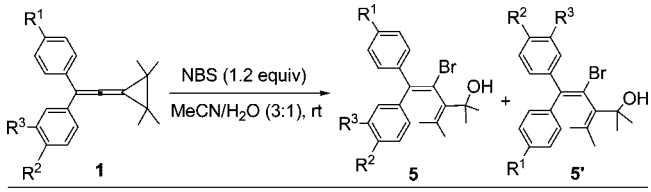
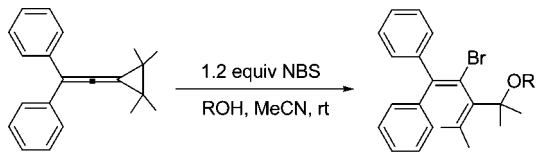
TABLE 2. Hydrobromination of Vinylidenecyclopropanes 1 by NBS and Water in MeCN

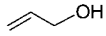
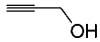


entry	substrate	R^1	R^2	R^3	time (min)	yield (%)[a] of **5** + **5′**
1	**1b**	Me	Me	H	10	**5b**, 96
2	**1c**	MeO	MeO	H	10	**5c**, 88
3	**1d**	Cl	Cl	H	30	**5d**, 76
4	**1e**	F	F	H	30	**5e**, 81
5[b]	**1f**	Me	H	H	10	**5f** + **5f′**, 93
6[b]	**1g**	MeO	H	H	10	**5g** + **5g′**, 78
7[b]	**1h**	H	Me	Me	10	**5h** + **5h′**, 82
8[b]	**1i**	Cl	H	H	20	**5i** + **5i′**, 78

[a] Isolated yield. [b] **5f**:**5f′** = 1:1, **5g**:**5g′** = 2:1, **5h**:**5h′** = 1:1, **5i**:**5i′** = 1:1.

TABLE 3. Alkoxybromination of Vinylidenecyclopropane 1a with ROH and NBS in MeCN



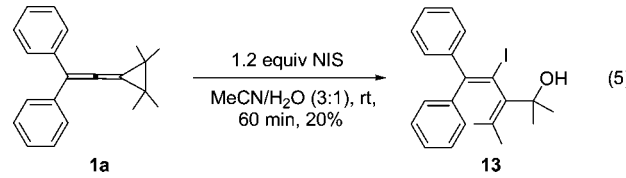
entry[a]	ROH	time	yield (%)[b] **6-12**
1	MeOH	30 min	**6**, 99
2	EtOH	5 h	**7**, 89
3	^{i}PrOH	12 h	**8**, 77
4		30 min	**9**, 78 (87[c])
5		2 h	**10**, 67
6		2 h	**11**, 67 (74[c])
7	^{t}BuOH	24 h	-
8[d]	AcOH	2 h	**12**, 42
9[d]	Ac_2O	2 h	**12**, 60

[a] Reaction conditions: VDCP (0.18 mmol), MeCN (1.0 mL), ROH (1.0 mL), NBS (1.2 equiv), rt. [b] Isolated yields. [c] VDCP (1.28 mmol), MeCN (1.5 mL), ROH (1.5 mL), NBS (1.2 equiv), rt. [d] 50 mg of MS 4Å was added.

10 min (Table 2, entries 1, 2, 5, 6, and 7). Adding moderately electron-withdrawing chloro or fluoro groups on the benzene rings of symmetrical vinylidenecyclopropanes **1d** and **1e** as well as unsymmetrical vinylidenecyclopropane **1i** afforded vinylbromohydrin derivatives **5d**, **5e**, and **5i** in moderate yields within 30 min (Table 2, entries 3, 4, and 8). As for unsymmetrical vinylidenecyclopropanes **1f**, **1g**, **1h**, and **1i**, the corresponding vinylbromohydrin derivatives **5f**−**i** were obtained as isomeric mixtures.

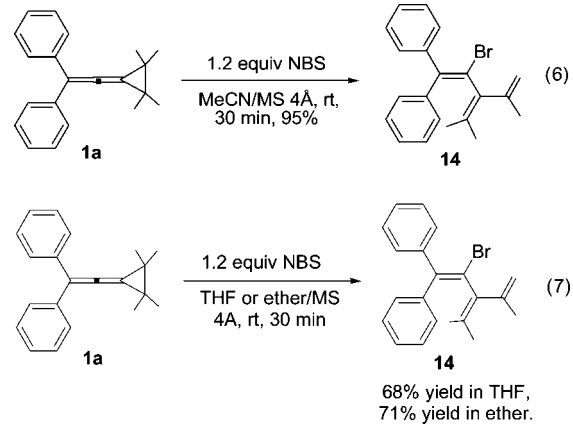
Encouraged by these results, we further investigated the reactivity of vinylidenecyclopropane **1a** with various alcohols and NBS in MeCN under the standard conditions and the results are summarized in Table 3. It was found that methoxybromination of **1a** by NBS and methanol proceeded smoothly within 30 min, affording the corresponding vinylbromomethoxy **6** in quantitative yield (Table 3, entry 1). Similarly, the alkoxybromionation of **1a** with ethanol and NBS gave the corresponding vinylbromoethoxy derivative **7** in 89% yield within 5 h (Table 3, entry 2). However, the alkoxybromionation of **1a** with isopropanol and NBS became more sluggish, affording the corresponding isopropoxy bromide **8** in 77% yield after 12 h, presumably due to the steric hindrance of the employed alcohol (Table 3, entry 3). Moreover, when the alkoxybromination of **1a** in the mixed solvent of *tert*-butyl alcohol and MeCN (1:1) with NBS was carried out under the standard conditions, none of the corresponding *tert*-butoxy bromide could be isolated, suggesting that the steric bulkiness of the employed alcohols plays a key role in this reaction (Table 3, entry 7). Other alcohols, such as allyl alcohol, benzyl alcohol, and propargyl alcohol, produced the corresponding alkoxy bromides **9**, **10**, and **11** in moderate yields under the standard conditions (Table 3, entries 4, 5, and 6). As for carboxylic acid or anhydride, such as acetic acid or acetic anhydride, the corresponding product **12** was obtained in 42% or 60% yields, respectively, under the standard conditions (Table 3, entries 8 and 9).

In addition, the reaction of *N*-iodosuccinimide (NIS) and **1a** in MeCN/water produced the corresponding vinyliodohydrin derivative **13** in 20% yield under the standard conditions. The reason the corresponding product **13** was isolated in low yield is because it decomposes during the purification on the silica gel column chromatography by heat and light (eq 5).



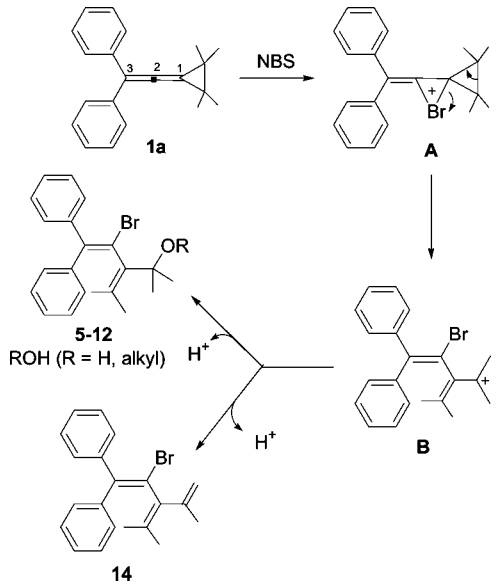
(5)

Interestingly, when molecular sieves 4Å was employed to remove the trace amounts of water in anhydrous MeCN, the brominated product **14** was obtained in 95% yield rather than vinylbromohydrin derivative **5a** if using **1a** as the substrate (eq 6).[9i] The similar examinations were also employed in dry THF and ether, providing **14** in 68% and 71% yields, respectively (eq 6).



A plausible mechanism for this hydrobromination or alkoxybromination of vinylidenecyclopropanes **1** (**1a** as the example) by NBS with water or alcohols is shown in Scheme 1. First, a three-membered cyclic bromonium ion intermediate **A** is formed by the electrophilic addition of Br^+ ion (generated from NBS)

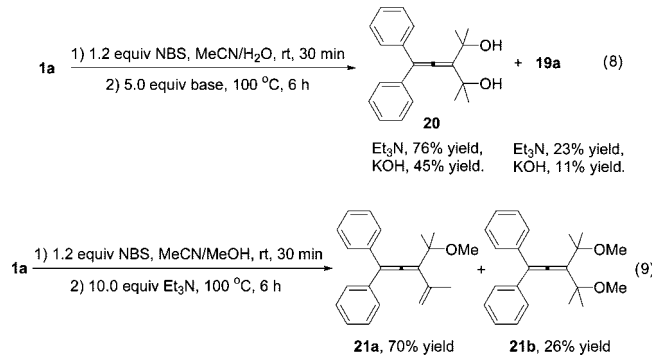
SCHEME 1. Proposed Mechanism for the Hydrobromination and Alkoxybromination of VDCPs 1 by NBS and ROH



onto **1a**,[4c,9i,15] which undergoes a ring-opening process to afford the corresponding cationic intermediate **B** due to the highly strained cyclopropane ring. Deprotonation of **B** furnishes the corresponding vinylbromo-1,3-diene derivative **14** in the absence of water. In the presence of nucleophilic reagents (such as H_2O or ROH), intermediate **B** undergoes a nucleophilic attack along with a deprotonation process to afford the corresponding hydrobromination derivative **5a** or alkoxybromination derivatives **6**−**12**. The regioselectivity can be explained by considering the fact that the C_2═C_3 double bond is more electron deficient than the C_1═C_2 double bond due to the presence of the two aromatic rings. Therefore, the C_1═C_2 double bond is preferential for the electrophilic addition of Br^+ ion to form the three-membered cyclic bromonium ion intermediate **A** (Scheme 1).

We also utilized other types of vinylidenecyclopropanes such as compound **15** in this reaction to obtain other types of vinylbromohydrins and alkoxybromides. In the presence of NBS and H_2O or NBS and methanol, **15** can be transformed rapidly to the corresponding vinylbromohydrin **16** in 56% yield or methoxybromide **17** in 47% yield within 10 min under the standard conditions, respectively. We attempted to remove the trace amount of ambient water in anhydrous MeCN with the addition of molecular sieves 4Å and subsequently performed the reaction under the standard conditions. However, compound **18** was obtained in 12% yield along with some other unidentified complex product mixtures (Scheme 2).[8t] This result suggested that the three-membered cyclic bromonium ion intermediate **A**, which was generated from vinylidenecyclopropane **15** with NBS, was attacked by nucleophilic reagent in the reaction system in an S_N2 pathway to give product **16** or **17**, and, in the absence of nucleophile, intermediate **A′** could be formed, which furnished compound **18** via intramolecular Friedel−Crafts reaction along with some other unidentified products via the other reaction pathways.

To extend the synthetic application of these vinylbromohydrins and alkoxybromides, we attempted to prepare α-allenic alcohols from these simple compounds. It was found that the vinylbromohydrins **5** can be transformed smoothly to the corresponding α-allenic alcohols **19** in excellent yields by removing a molecule of hydrobromide in the presence of Et_3N in DMF at 100 °C as shown in Table 4. We also attempted to obtain the corresponding α-allenic alcohol **19a** solely from **1a** in a one-pot manner by adding Et_3N or KOH as base in a sealed tube. However, it was found that a diol product **20** was formed in 76% or 45% yield along with **19a** in 23% yield or 11% yield due to the presence of water in the reaction system, respectively (eq 8). When methanol was employed as the cosolvent instead of water in acetonitrile, the α-allenic ethers **21a** and **21b** also could be obtained in 70% and 26% yields, respectively (eq 8).



α-Allenic alcohols have drawn much attention in organic synthesis because of their unique reactivities and the ease on

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SCHEME 2. Reactions of Vinylidenecyclopropane 15 with NBS in MeCN

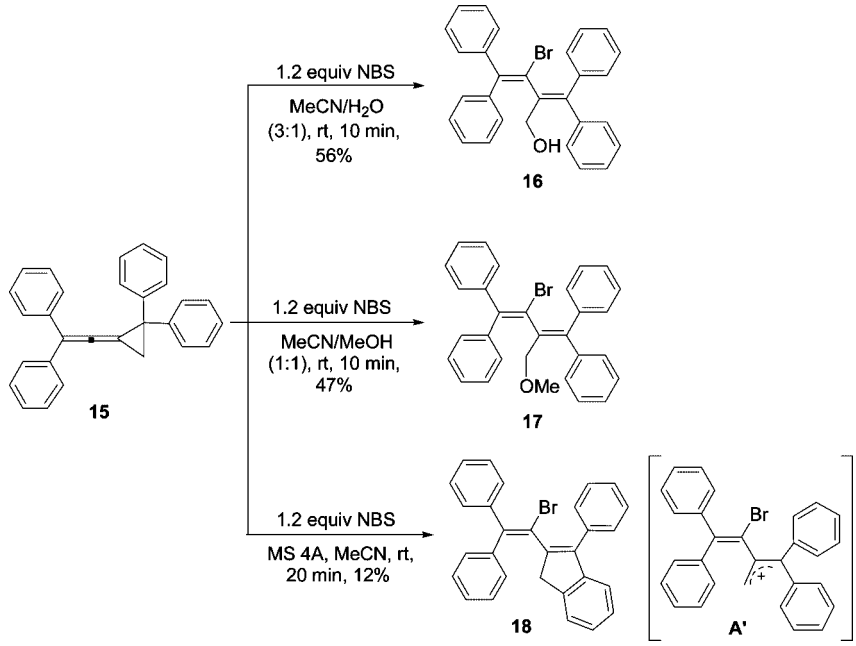
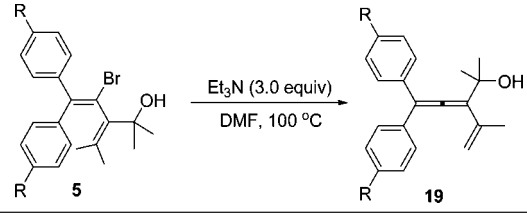


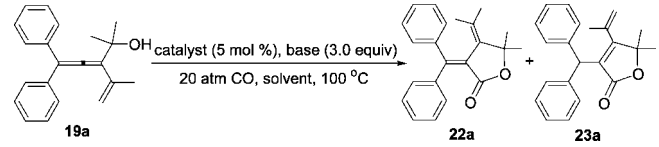
TABLE 4. Preparation of α-Allenic Alcohols 19 from Vinylbromohydrins 5 in the Presence of Et_3N



entry[a]	R	time (h)	yield (%)[b] of **19**
1	H, **5a**	4	**19a**, 99
2	Me, **5b**	3	**19b**, 90
3	Cl, **5c**	3	**19c**, 90

[a] General procedure: 0.10 mmol of **5** and 0.30 mmol of base in 2 mL of DMF were stirred at 100 °C. [b] Isolated yield.

TABLE 5. Cyclocarbonylation of α-Allenic Alcohol 19a with CO Catalyzed by Various Metal Complexes



					yield(%)[b]	
entry[a]	catalyst	base	solvent	time (h)	**22a**	**23a**
1	$Ru_3(CO)_{12}$	Et_3N	dioxane	12		
2	$Ru_3(CO)_{12}$	Et_3N	DMF	12		
3	$PdCl_2$	K_2CO_3	DMF	33		
4[c]	$Pd(OAc)_2$		DMF	48		
5[c]	$PtCl_2$		DMF	28		
6[c]	$PdCl_2$		DMF	48	68	23

[a] General procedure: 0.1 mmol of **19a,** 5 mol % of catalyst, and 0.30 mmol of base in 3 mL of DMF were stirred at 100 °C under 20 atm CO. [b] Isolated yield. [c] No base was used.

the further transformation into novel compounds with other functional groups in allenic chemistry.[16,17a] However, there have been few reports so far on the cyclocarbonylation of α-allenic alcohols to form lactones in the literature.[18] Subsequently, we attempted to examine the cyclocarbonylation of these α-allenic alcohols using metal catalysts under CO atmosphere. Initially, we examined a standard reaction of **19a** (0.10 mmol) under 20 atm of carbon monoxide in the presence of $Ru_3(CO)_{12}$ complex (0.005 mmol) and Et_3N (0.30 mmol) in 1,4-dioxane (3 mL) at 100 °C for 12 h. None of the corresponding lactone was formed along with the recovery of 93% of starting materials **19a** (Table 5, entries 1 and 2). Next, we examined other metal catalysts such as $PdCl_2$ (with K_2CO_3), $Pd(OAc)_2$, and $PtCl_2$ in this reaction, but all of them did not have catalytic abilities for the cyclocarbonylation of **19a** (Table 5, entries 3−5). Delightfully, using $PdCl_2$ as a catalyst in the absence of base afforded the corresponding cyclocarbonylation reaction product **23a** and **22a** as a pair of isomeric mixtures in 68% and 23% yields, respectively (Table 5, entry 6). The structure of **23a** was unambiguously determined by X-ray diffraction and its CIF data are presented in the Supporting Information.[19]

We realized that the isomeric mixtures of 2(3*H*)-dihydrofuranone **22a** or 2(5*H*)-furanone **23a** could be transformed from one to another by a 1,5-*H* transfer, which might occur at higher temperature in the presence of metal complex (Table 5, entry 6).[18b] Therefore, we next anticipated to obtain **22a** or **23a** solely by changing the reaction conditions. It was found that reducing the reaction time to 6 h with $PdCl_2$ (5 mol %) as a catalyst at 100 °C afforded 2(3*H*)-dihydrofuranone **22a** solely in 31% yield (Table 6, entry 1). Extending the time to 9 and 12 h produced **22a** solely in 53% and 50% yields, respectively (Table 6, entries 2 and 3). The two isomers were both obtained again when the reaction time was extended to 75 h, and **22a** became the minor

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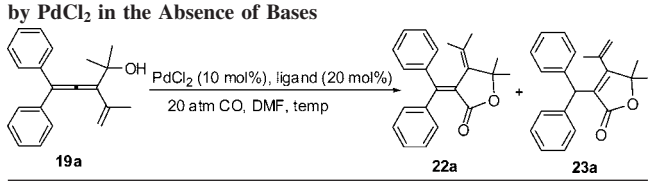
(19) The crystal data of **23a** have been deposited in CCDC as no. 662541. Empirical formul: $C_{22}H_{22}O_2$; formula weight: 318.40; crystal color, habit: colorless, prismatic; crystal dDimensions: 0.498 × 0.357 × 0.311 mm^3; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 11.6537(18) Å, b = 14.736(2) Å, c = 11.9299(18) Å, α = 90°, β = 119.237(2)°, γ = 90°, V = 1787.7(5) Å^3; space group: $P2(1)/c$; Z = 4; D_{calc} = 1.183 g/cm^3; F_{000} = 680; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0511, 0.1346.

TABLE 6. Cyclocarbonylation of α-Allenic Alcohol 19a Catalyzed by $PdCl_2$ in the Absence of Bases



				yield (%)[b]	
entry[a]	ligand	temp (°C)	time (h)	**22a**	**23a**
1	*c*	100	6	31	trace
2	*c*	100	9	53	trace
3	*c*	100	12	50	trace
4	*c*	100	75	3	53
5	PPh_3	120	100	*d*	60
6	dppb	120	100	*d*	57
7	*c*	150	28	*d*	72
8	PPh_3	150	28	*d*	57
9	dppp	150	28	complex	
10	*c*	70	28	no reaction	
11	PPh_3	70	28	63	*d*
12	dppp	70	28	70	*d*

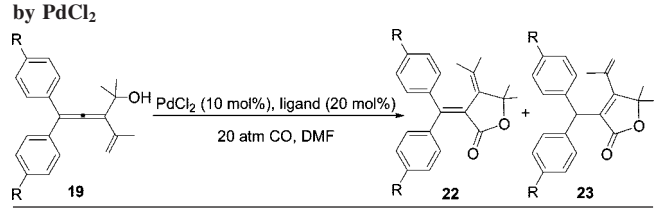
[a] General procedure: 0.1 mmol of **19a,** 10 mol % of catalyst, and 20 mol % of ligand in 3 mL of DMF were stirred under 20 atm CO. [b] Isolated yield. [c] No ligand was used. [d] None of the product was isolated.

product in only 3% yield along with 2(5*H*)-furanone **23a** in 53% yield (Table 6, entry 4). Adding phosphine ligands such as PPh_3 and 1,4-bis(diphenylphosphino)butane (dppb), enhancing the temperature, and extending the reaction time facilitated the formation of **23a** (Table 6, entries 5 and 6). To reduce the reaction time, we raised the reaction temperature to 150 °C, and found that product **23a** was obtained solely in 72% yield in the absence of ligand and in 57% yield in the presence of PPh_3 within 28 h, respectively, although using 1,3-bis(diphenylphosphino)propane (dppp) as a ligand afforded complex product mixtures under otherwise identical conditions, suggesting that **23a** might be derived from **22a** upon heating at >100 °C (Table 6, entries 7−9). Encouraged by these results, we also attempted to obtain **22a** solely at lower temperature. When the temperature was turned down to 70 °C, no reaction occurred in the presence of $PdCl_2$ (Table 6, entry 10). However, we were pleased to find that product **22a** could be obtained in good yields (63% and 70%) by adding PPh_3 or 1,3-bis(diphenylphosphino)-propane (dppp) as a ligand at 70 °C within 28 h (Table 6, entries 11 and 12). These results can be explained by the fact that CO insertion into a Pd−C bond occurs more rapidly for those alkylpalladium phosphine complexes.[20a]

According to the above results, we turned our attention to examine the generality of the present catalytic system using α-allenyl alcohols **19b** and **19c** that contain electron-donating groups and electron-withdrawing groups on the benzene rings, respectively, and the results of these experiments are summarized in Table 7. In the presence of $PdCl_2$ and dppp, the cyclocarbonylation of **19b** and **19c** proceeded smoothly at lower temperature (70 and 80 °C) to give the corresponding lactones **22b** and **22c** in moderate yields (Table 7, entries 1 and 2). On the other hand, in the absence of ligand, the cyclocarbonylation of **19b** and **19c** catalyzed by $PdCl_2$ at 150 °C afforded the

(20) (a) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598–1603. (b) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1992**, *430*, 357–372.

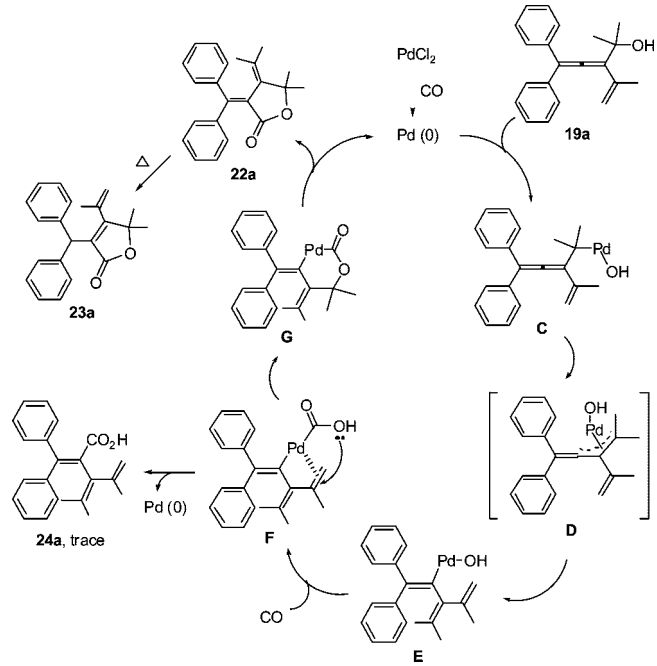
TABLE 7. Cyclocarbonylation of α-Allenic Alcohols 19 Catalyzed by $PdCl_2$



					yield (%)[b]	
entry[a]	R	ligand	temp (°C)	time (h)	**22**	**23**
1	Me, **19b**	dppp	70	28	**22b**, 61	*d*
2	Cl, **19c**	dppp	80	30	**22c**, 62	*d*
3	Me, **19b**	*c*	150	28	*d*	**23b**, 74
4	Cl, **19c**	*c*	150	28	*d*	**23c**, 75

[a] General procedure: 0.1 mmol of **19,** 10 mol % of catalyst, and 20 mol % of ligand in 3 mL of DMF were stirred under 20 atm CO. [b] Isolated yield. [c] No ligand was used. [d] The product was not detected.

SCHEME 3. Proposed Mechanism for the Cyclocarbonylation of α-Allenic Alcohols19



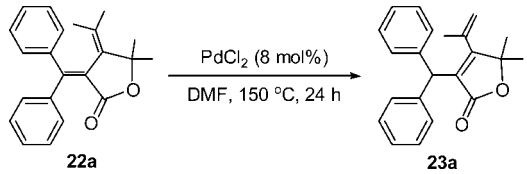
corresponding lactones **21b** and **21c** in good yields (Table 7, entries 3 and 4). Therefore, using the phosphine ligand and changing the reaction temperature and reaction time, the selective cyclocarbonylation of α-allenic alcohols **19** could be realized in the presence of $PdCl_2$.

A possible mechanism for the cyclocarbonylation of α-allenic alcohols (**19a** as the example) is outlined in Scheme 3. Palladium(0), generated from Pd(II) and carbon monoxide, can insert into the C−O bond of **19a** to give intermediate **C** via oxidative addition,[21a,22a] which can further form the alkenylpalladium intermediate **E** via allylpalladium intermediate **D**. The oxidative addition of Pd(0) complexes to allylic alcohols to form

(21) (a) Piotti, M. E.; Alper, H. *J. Org. Chem.* **1994**, *59*, 1956–1957. (b) Yu, W.-Y.; Alper, H. *J. Org. Chem.* **1997**, *62*, 5684–5687. (c) Xiao, W.-J.; Alper, H. *J. Org. Chem.* **2005**, *70*, 1802–1807.

(22) Some other examples of insertion of carbon monoxide into carbon−heteroatom bonds catalyzed by palladium complexes: (a) Crudden, C. M.; Alper, H. *J. Org. Chem.* **1995**, *60*, 5579–5587. (b) Imada, Y.; Nishimura, K.; Murahashi, S.-I. *Tetrahedron* **1994**, *50*, 453–464. (c) Imada, Y.; Alper, H. *J. Org. Chem.* **1996**, *61*, 6766–6767.

SCHEME 4. A Control Experiment on the Transformation of 22a to 23a in the Presence of $PdCl_2$



under 20 atm of CO atmosphere, 89% yield,
under ambient atmosphere, 82% yield.

allylpalladium complexes has been proposed by Trost and Verhoeven,[23] and the same type of intermediate like **D**, where the π-allyl group is directly attached to the double bond, has been suggested for the reaction of allenyl esters and carbonates using Pd(0) catalysts.[24] The formation of the conjugate diene would be the driving force for the conversion of the π-bonded complex **D** to the σ-bonded complex **E**.[21a] The insertion of CO into the Pd−OH bond produces intermediate **F**, which generates a cyclopalladium complex **G** by an intramolecular oxidative addition of OH to the double bond. This may explain why the cyclocarbonylation cannot occur in the presence of base because NEt_3 or K_2CO_3 can inhibit the intramolecular oxidative addition of OH to the double bond in intermediate **F** by forming a salt. Moreover, the existence of intermediate **F** can be proved by the isolation of trace amount of acid **24a** in a large scale cyclocarbonylation of **19a**,[25] which should be derived from the reductive elimination of intermediate **F**. The double bond at the γ-position of Pd is essential for the cyclocarbonylation of **19a** to be able to take place since many other types of α-allenic alcohols cannot undergo such a cyclocarbonylation in the presence of palladium complexes under similar conditions.[18,23] The reductive elimination of intermediate **G** gives the corresponding lactone product 2(3*H*)-dihydrofuranone **22a** and regenerates the Pd(0) species. 2(3*H*)-Dihydrofuranone **22a** can be transformed to the corresponding 2(5*H*)-furanone **23a** in the presence of palladium complex at higher temperatures (100−150 °C) via a 1,5-*H* transfer (Scheme 3). This transformation is proved in a control experiment by employing 2(3*H*)-dihydrofuranone **22a** and $PdCl_2$ (8 mol %) in DMF at 150 °C under CO atmosphere or ambient atmosphere, affording the corresponding 2(5*H*)-furanone **23a** in 89% or 82% yield, respectively (Scheme 4). It also should be noted that upon heating at 150 °C, **22a** could not be transformed to **23a**, suggesting that $PdCl_2$ is essential in this transformation.

Conclusion

We have disclosed in this paper that the hydrobromination or alkoxybromination of vinylidenecyclopropanes **1** could be achieved in the presence of NBS and water or alcohols under mild conditions. By this synthetic approach, the corresponding vinylbromohydrin derivatives **5** or vinylbromoalkoxy derivatives **6**−**12** can be obtained in moderate to excellent yields. A considerable range of aromatic groups-substituted VDCPs **1** has been examined in the reaction, providing an efficient route to the synthesis of various vinylbromohydrin or vinylbromoalkoxy derivatives according to different substrates. These vinylbromohydrin derivatives **5** can be easily transformed to α-allenic alcohols **19** in the presence of Et_3N. In addition, the cyclocarbonylation of α-allenic alcohols **19** with CO catalyzed by palladium chloride to give lactones **22** or **23** under different reaction conditions has been described. Efforts are underway to elucidate the mechanistic details and the scope and limitations of these reactions in the laboratory.

Experimental Section

General Remarks. ^{1}H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Infrared spectra were measured on a spectrometer. Mass spectra were recorded by the EI method, and HRMS was measured on a Kratos Analytical Concept mass spectrometer (EI or MALDI). Satisfactory CHN microanalyses were obtained with an analyzer. Melting points are uncorrected. All reactions were monitored by TLC with silica gel coated plates. Flash Column Chromatography was carried out with 300−400 mesh silica gel at increased pressure.

General Procedure for the Synthesis of Vinylbromohydrins. To a solution of vinylidenecyclopropanes (0.18 mmol) in MeCN (1.8 mL) was added 0.6 mL of water with a syringe. Then, 40 mg of NBS (1.2 equiv, 0.22 mmol) was added in one portion and the mixture was stirred for another 10 min at room temperature. The reaction mixture was quenched by addition of 10 mL of water then extracted with ether (3 × 10 mL), and the combined organic phases were washed with brine (1 × 20 mL) and dried over anhydrous $MgSO_4$. The products were purified by flash column chromatography with petroleum ether−EtOAc (5%).

4-Bromo-2-methyl-5,5-diphenyl-3-(propan-2-ylidene)pent-4-en-2-ol, 5a. A white solid, mp 108−110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.23 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.59 (s, 1H, OH), 1.94 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 7.18−7.38 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.7, 25.0, 30.3, 30.4, 72.9, 124.0, 127.3, 127.4, 127.9, 128.1, 128.4, 129.1, 137.4, 140.0, 140.6, 141.2, 143.2. IR (CH_2Cl_2) ν 3080, 3027, 2928, 2853, 1730, 1628, 1596, 1492, 1443, 1371, 1277, 1120, 1074, 1031, 965, 900, 790, 771, 758, 745, 697, 597, 567 cm^{-1}. MS (%) *m/e* 353 ($M^+ - H_2O$, 1), 290 ($M^+ - Br$, 6), 273 ($M^+ - Br - H_2O$), 233 (29), 232 (100), 217 (36), 215 (26), 202 (18), 91 (17), 59 (26). HRMS (EI) for $C_{21}H_{21}Br$ ($M - H_2O$) 352.0827, found 352.0825. Anal. Calcd for $C_{21}H_{23}OBr$: C, 67.93; H, 6.24. Found: C, 67.99; H, 6.20.

General Procedure for the Synthesis of α-Allenic Alcohols. To a solution of **5** (0.10 mmol) in DMF (3.0 mL) was added 3.0 equiv of Et_3N with a syringe, and the resulting mixture was stirred for 3−4 h at 100 °C, followed by addition of water (5 mL), and extracted with ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 20 mL) and dried over anhydrous $MgSO_4$. The products were purified by a flash column chromatography with petroleum ether−EtOAc (5%).

2-Methyl-5,5-diphenyl-3-(prop-1-en-2-yl)penta-3,4-dien-2-ol, 19a. A white solid, mp 124−126 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.56 (s, 6H, $2CH_3$), 1.95 (s, 3H, CH_3), 5.15 (dd, J = 1.2 Hz, J = 1.5 Hz, 1H), 5.46 (s, 1H), 7.25−7.35 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.6, 30.5, 72.4, 111.9, 115.4, 118.3, 127.2, 128.1, 128.5, 136.6, 137.8, 204.3. IR (CH_2Cl_2) ν 3568, 3448, 2974, 2928, 1919, 1616, 1597, 1492, 1449, 1375, 1173, 1106, 1030, 900, 827, 767, 695, 636, 577, 550 cm^{-1}. MS (%) *m/e* 290 (M^+, 8), 257 (11), 232 (100), 217 (69), 202 (30), 189 (12), 165 (17), 59 (58), 43 (54). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.55; H, 7.88.

General Procedure for the Cyclocarbonylation of α-Allenic Alcohols Catalyzed by $PdCl_2$ to Give 2(3*H*)-Furanones. To a solution of **19** (0.10 mmol) in DMF (3.0 mL) were added $PdCl_2$ (10 mol%) and dppp (20 mol%), and the resulting mixture was stirred for 28 h at 70−80 °C under 20 atm of carbon monoxide. The reaction was quenched by addition of water (5 mL) and

(23) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730–4743, and references cited therein.

(24) Nokami, J.; Maihara, A.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 5629–5630.

(25) A trace of acid **22a** can be obtained in a large scale cyclocarbonylation with use of 0.3 mmol of **18a** under the standard conditions.

extracted with ether (3 × 10 mL), and the combined organic phases were washed with brine (1 × 20 mL) and dried over anhydrous $MgSO_4$. The products were purified by a flash column chromatography with petroleum ether−EtOAc (10%).

3-(Diphenylmethylene)-5,5-dimethyl-4-(propan-2-ylidene)-dihydrofuran-2(3*H*)-one, 22a. A light yellow solid, mp 128−130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.05 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.71 (s, 6H, $2CH_3$), 7.11−7.14 (m, 2H, Ar), 7.24−7.38 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 22.1, 24.7, 27.2, 83.9, 123.7, 127.3, 128.3, 128.5, 128.9, 129.8, 130.6, 131.3, 135.6, 140.1, 143.6, 152.6, 167.7. IR (CH_2Cl_2) ν 3057, 2976, 2926, 2853, 1757, 1490, 1444, 1368, 1283, 1246, 1202, 1091, 1070, 1009, 941, 762, 753, 697, 652, 590 cm^{-1}. MS (%) *m*/*e* 318 (M^+, 16), 303 (18), 257 (66), 245 (51), 215 (33), 199 (100), 165 (13), 105 (41), 77 (39). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.68; H, 6.93.

3-(Di-*p*-tolylmethylene)-5,5-dimethyl-4-(propan-2-ylidene)dihydrofuran-2(3*H*)-one, 22b. A light yellow solid, mp 114−116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.05 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.70 (s, 6H, $2CH_3$), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.01 (d, J = 8.1 Hz, 2H, Ar), 7.07 (d, J = 8.1 Hz, 2H, Ar), 7.25 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 21.5, 22.1, 24.7, 27.2, 83.7, 122.6, 128.0, 129.1, 129.6, 129.9, 131.4, 136.0, 137.4, 138.3, 139.0, 140.8, 153.0, 168.0. IR (CH_2Cl_2) ν 3023, 2976, 2924, 2859, 1747, 1650, 1605, 1510, 1463, 1371, 1253, 1188, 1089, 1069, 1036, 1010, 926, 824, 804, 734, 537 cm^{-1}. MS (%) *m*/*e* 346 (M^+, 51), 331 (58), 313 (15), 288 (19), 273 (100), 260 (11), 245 (14), 229 (12), 213 (15). HRMS (EI) for $C_{24}H_{26}O_2$ 346.1933, found 346.1936.

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Supporting Information Available: Detailed experimental procedures, ^{1}H and ^{13}C NMR spectroscopic data for vinylbromohydrin derivatives **5** and vinylbromoalkoxy derivatives **6**-**12**, compounds **14**, **16**-**18**, α-allenic alcohols **19** and **20** as well as the lactone products **22** and **23**, X-ray crystal structure of **23a**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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