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Preparation of alkylidene cyclic carbonates via cyclization of propargylic carbonates

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Abstract

α-Alkylidene cyclic carbonates have been prepared according to the general strategy to cyclize propargylic carbonates in the presence of an appropriate catalyst such as K_2CO_3-crown ether or a palladium complex.

Keywords: Carbon dioxide; Palladium; α-Alkylidene cyclic carbonate; Propargyl alcohol

1. Introduction

α-Alkylidene cyclic carbonates are of interest as functional carbonates in the preparation of β-oxopropyl carbonates [1], furanones [2], dihydrofuranones [3], oxatrimethylenemethane–palladium [4] and ketoalcohols [5]. One approach obtaining these cyclic carbonates is the utilization of propargylic alcohol derivatives and CO_2 as the starting materials. This strategy is fundamentally based on the cyclization of the propargylic carbonate species ($HC{\equiv}CCH_2OCO_2-$) into the corresponding α-alkylidene cyclic carbonate in the presence of a catalyst such as ruthenium [6], cobalt [7], palladium [5,8], copper [9–13], or phosphine [14].

In this paper we report that K_2CO_3-crown ether is another effective catalyst for the preparation of α-alkylidene cyclic carbonate starting from propargylic alcohol and CO_2. And also reported is that palladium(0) complexes can be used as catalyst for the transformation of specific propargylic carbonate substrates into the corresponding α-alkylidene cyclic carbonates.

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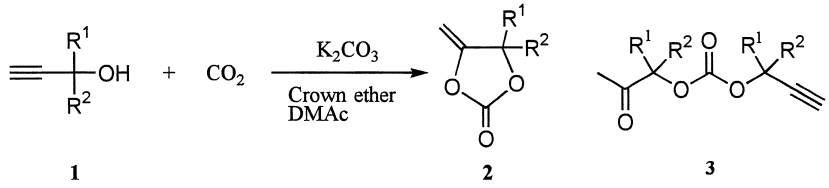
2. Results and discussion

2.1. Preparation of α-alkylidene cyclic carbonates catalyzed by K_2CO_3-crown ether

The reaction of propargylic alcohol **1** and CO_2 (0.5 MPa) was performed at 80°C in *N,N*-dimethylacetamide (DMAc) in the presence of a catalytic amount of K_2CO_3 (0.25 equiv.) and dibenzo-18-crown-6 ether (0.4 equiv. to K_2CO_3).



1 **2** **3**

Since K_2CO_3 dissolves in DMAc only sparingly, the reaction is heterogeneous. The representative results are given in Table 1. α-Methylene cyclic carbonates **2** were obtained in reasonable yields with tertiary propargylic alcohols (R^1, R^2 = alkyl or aryl). β-Oxopropyl carbonates **3** were also produced concomitantly in limited amounts (~7%), which arose from further reaction of **2** with **1** [1]. The nature of the substituents R^1 and R^2 decidedly effects the reaction. Thus secondary and primary propargylic alcohols did not give cyclic carbonates. So the reaction seems to be specific for tertiary alcohols. The yields in the absence of the crown ether dropped considerably (for **2a**, 78% → 67%). This effect of the crown ether may be accounted for the coordination of the cation K^+ to leave the carbonate ion ($HC{\equiv}CCR^1R^2OCO_2^-$) freer making the cyclization easier. Tetrabutylphosphonium bromide (0.4 equiv. to K_2CO_3) can be used as an effective additive [15,16] instead of the crown ether without a solvent to yield **2a** in 61% under an atmospheric pressure of CO_2. Bases other than K_2CO_3 were tested. Rb_2CO_3, Cs_2CO_3 and K_3PO_4 could be used equally well but Li_2CO_3, Na_2CO_3, $KHCO_3$, Et_3N and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) afforded **2a** in only 0 ~ 9% yield [17,18]. It is clear that not only the basicity but also the kind of cation affects the reaction.

The pressure of CO_2 also influences the reaction. Although the reactions could be conducted under an atmospheric pressure of CO_2 instead of 0.5 MPa, the yields declined fairly (for **2a**, 78% → 64%). The reaction under N_2 atmosphere did not proceed at all indicating that the CO_2 moiety in **2** came

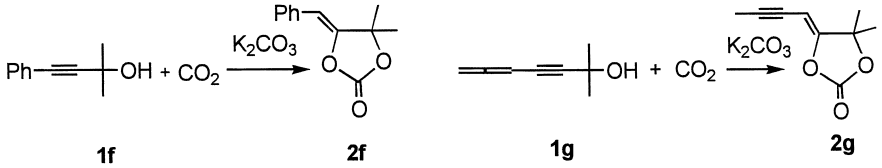
Table 1
Synthesis of cyclic carbonate **2** from propargyl alcohol **1** and CO_2 [a]

Alcohol 1	Substituent	Carbonate **2**	Yield (%)[b]
1a	$R^1 = R^2 = Me$	**2a**	(78)
1a[c]	$R^1 = R^2 = Me$	**2a**	(61)
1b	$R^1 = Me$, $R^2 = Et$	**2b**	65
1c	$R^1 = Me$, $R^2 = Pr^i$	**2c**	69
1d	$R^1–R^2 = –(CH_2)_5–$	**2d**	75
1e	$R^1 = Me$, $R^2 = Ph$	**2e**	50

[a] Reaction conditions: 2 mmol **1**; 0.5 mmol K_2CO_3; 0.2 mmol dibenzo-18-crown-6-ether; 4 cm^3 DMAc; 0.5 MPa CO_2; 80°C; 5 h.
[b] The figures in parentheses are GLC yields.
[c] The reaction was performed without solvent under an atmospheric pressure of CO_2 employing 0.2 mmol of Bu^n_4PBr instead of the crown ether.

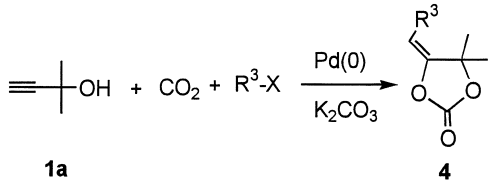
from CO_2 gas directly not from K_2CO_3. The choice of solvent is also important. Polar aprotic solvents such as *N,N*-dimethylformamide and 1-methyl-2-pyrrolidone were suitable as well. The reaction stopped completely in propionitrile or 1,4-dioxane.

The preparation of alkylidene cyclic carbonates was not feasible with alkyl substituted propargylic alcohols like $MeC{\equiv}CCMe_2OH$, *n*-$BuC{\equiv}CCMe_2OH$, or *tert*-$BuC{\equiv}CCMe_2OH$. But when the substrate has an unsaturated conjugated group, cyclic carbonate is produced. Thus 2-methyl-4-phenylbut-3-yn-2-ol **1f** gave the corresponding carbonate (*Z*)-**2f** in 35% isolated yield after 5 h reaction at 80°C under an atmospheric pressure of CO_2 in DMAc without the crown ether. 2-Methylhept-3-yn-5,6-diene-2-ol **1g** afforded the cyclized carbonate (*Z*)-**2g** in 15% isolated yield after 5 h reaction at 80°C under an atmospheric pressure of CO_2 in DMAc without the crown ether where the dienyl group in **1g** isomerized into the propynyl group in **2g**.



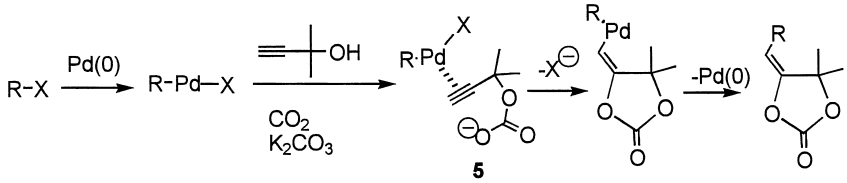
2.2. Preparation of cyclic carbonates catalyzed by palladium(0)

Since alkylidene cyclic carbonates were not obtained from alkyl group-substituted propargylic alcohols (vide supra), palladium-mediated incorporation of an alkyl group onto the double bond in the product during cyclization was investigated. Heating a mixture of propargylic alcohol **1a**, methyl iodide and K_2CO_3 in the presence of a catalytic amount of $Pd(OAc)_2$ and PPh_3 at 100°C in acetonitrile under CO_2 pressure, ethylidene cyclic carbonate (*E*)-**4a** (R^3 = Me) was formed in 64% GLC yield stereoselectively.



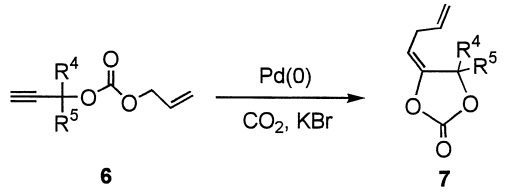
Similarly, allyl bromide, phenyl iodide and benzyl bromide afforded the corresponding cyclic carbonates **4b** (R^3 = allyl), **4c** (R^3 = Ph) and **4d** (R^3 = benzyl) in 47% (*E:Z* = 92:8), 38% (*E:Z* = 100:0) and 58% (*E:Z* = 100:0) isolated yield, respectively. It is noted that the benzylidene cyclic carbonate **4c** obtained by this method and the one **2f** obtained from **1f** and CO_2 (vide supra) are opposite in stereochemistry. The formation of the cyclic carbonate was not possible with ethyl bromide and *n*-propyl bromide. Utimoto et al. have reported the $PdCl_2(CH_3CN)_2$-catalyzed carboxylative coupling of lithium propargylic alcoholate with allyl chloride [5]. In this case, however, the reaction is not applicable to the propargyl alcohol containing a terminal acetylenic group.

The presumed reaction pathway is depicted as follows.



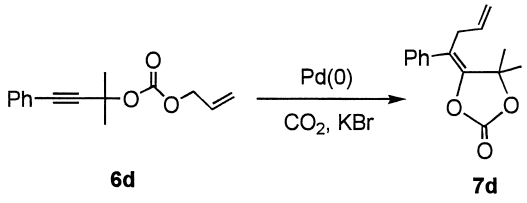
The attack of the carbonate ion on the triple bond in the key intermediate **5** takes place from the outside of the metal to afford the (*E*)-product stereoselectively [5]. Since the oxidative addition process of alkyl halide to form the metal–alkyl bond is involved in the reaction pathway, ethyl and *n*-propyl bromides are not suitable substrates which experience β-hydrogen elimination.

Palladium(0)-promoted another approach to alkylidene cyclic carbonates is the utilization of allylic propargylic carbonates as the starting material. Several transformations of allylic carbonates are known to be mediated by palladium complexes. The first step is the oxidative addition of these substrates to yield allylic palladium carbonate species. Then facile decarboxylation of the carbonate takes place to generate an allylic palladium alkoxide species [19]. According to the general strategy to cyclize a propargylic carbonate species into an α-alkylidene cyclic carbonate, several allylic propargylic carbonates **6** were subjected to the transformation under high pressure of CO_2 in order not to suffer decarboxylation.



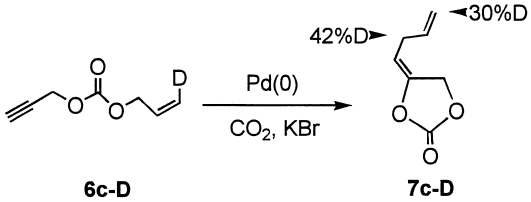
Treatment of allyl 1,1′-dimethylprop-2-ynyl carbonate **6a** (R^4, R^5 = Me) with a catalytic amount of $Pd(dba)_2$ [dba = dibenzylideneacetone] and $P(OPh)_3$ in the presence of KBr at 90°C in acetonitrile under high pressure of CO_2 afforded a cyclized product, 4-(3-butenylidene)-5,5-dimethyl-1,3-dioxolan-2-one (**7a**: $R^4 = R^5$ = Me) in a GLC yield of 79% (*E:Z* = 91:9). It is noted that the cyclic carbonate **7a** is identical with **4b**. The reaction under either an atmospheric pressure of CO_2 or N_2 proceeded only scarcely indicating the crucial effect of CO_2 pressure. When the reaction was carried out in THF or benzene, the rate of the reaction was severely retarded (yield 1 ~ 5%). The yield of **7a** declined considerably to 64% (*E:Z* = 82:18) without added inorganic salt. In addition to KBr, alkaline metal bromides like NaBr, RbBr and CsBr were effective to afford **7a** in 72, 80 and 81% yield, respectively, whereas addition of LiBr completely suppressed the reaction. The phosphorus ligand also exerted significant effects. Thus $P(OEt)_3$, PPh_3 and diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ (n = 2 and 3) were less effective for this cyclization process, producing **7a** in 1 ~ 20% yields. Bulkier tri(*o*-tolyl)phosphite proved suitable, forming **7a** in 85% yield (*E:Z* = 86:14). The yields of the products were profoundly effected by the nature of the substituent R^4 and R^5. The reaction with secondary propargylic compound (**6b**: R^4 = H, R^5 = Me) proceeded somewhat sluggishly giving the

cyclic carbonate **7b** in 54% yield ($E:Z = 97:3$). Primary substrate **6c** ($R^4 = R^5 = H$) gave **7c** in 27% yield ($E > 90\%$). This methodology opens a novel approach to alkylidene cyclic carbonates **7** formally resulting from secondary alcohols or propargyl alcohol itself, which cannot be obtained via direct reaction of CO_2. The reaction stopped with alkyl substitution (Me and *n*-butyl) at the terminal position of the triple bond. When a phenyl group is substituted on the triple bond, on the other hand, the reaction proceeded reluctantly giving the corresponding cyclic carbonate (*Z*)-**7d** in 37% isolated yield stereoselectively. The *Z*-structure was confirmed by the observation of NOE between the methyl and the internal methylene groups.



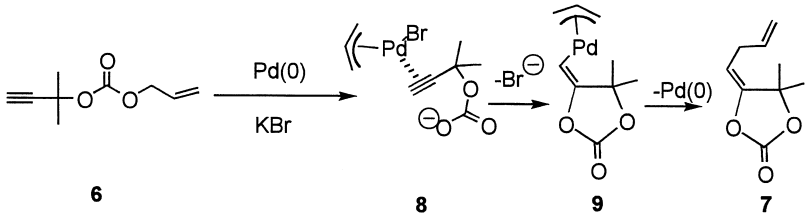
6d **7d**

In order to get some information about the mechanism, a deuterated substrate, 3-deuterio-2-propenyl 2-propynyl carbonate **6c**-D ($E:Z = 15:85$), was subjected to the palladium-catalyzed cyclization. This reaction gave 3-butenylidene cyclic carbonate **7c**-D in 12% isolated yield. ^{1}H-NMR measurement showed that the deuterium was scrambled on the C2 (42%) and C4 (30%) carbons.



6c-D **7c-D**

This result indicates that the reaction proceeds via a η^3-allyl palladium species. A presumed mechanism is outlined in Scheme 1. Oxidative addition of **6** to a palladium(0) species in the presence of bromide ion affords η^3-allylpalladium bromide intermediate **8** which is coordinated with propargyl carbonate ion. The intramolecular cyclization of coordinated propargyl carbonate into a vinylic palladium species **9** would occur. Reductive elimination takes place to give the observed product **7**.



6 **8** **9** **7**

The procedure reported herein offers facile preparation of several alkylidene cyclic carbonates through the general strategy to cyclize propargyl carbonate substrates.

3. Experimental

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC-250 or a DPX-400 spectrometer in $CDCl_3$. Chemical shifts (δ) are given in ppm and coupling constant (J) in Hz. IR spectra were recorded on a JASCO FT/IR-350 spectrometer. Mass spectra were performed at 70 eV with a Shimazu GCMS-QP2000 spectrometer. Melting points are uncorrected.

Propargyl alcohol derivatives **1a**–**e** were commercially available and used without further purification. Compound **1f** was prepared from lithium acetylide and acetone according to a general method [20]. Compound **1g** was synthesised from **1a** and propargyl chloride according to the literature method [20]. Allylic propargylic carbonates **6a**–**d** were prepared from lithium alkoxides and allyl chloroformate according to a general method [20].

*3.1. Preparation of α-alkylidene cyclic carbonate **2a**–**e** from propargylic alcohol **1a**–**e** and CO_2*

The propargylic alcohol **1** (2 mmol), K_2CO_3(0.5 mmol), dibenzo-18-crown ether (0.2 mmol) and DMAc (4 cm^3) were charged in an autoclave, into which CO_2 was introduced up to 0.5 MPa. The autoclave was heated at 80°C for 5 h. After the reaction, the reaction mixture was taken up in 20 cm^3 diethyl ether. Then 20 cm^3 of 1 M HCl was added to the mixture. The organic layer was separated, dried over $MgSO_4$ and concentrated. The carbonates **2a**–**e** were isolated by silica gel column chromatography eluting with hexane–chloroform (1:1). Carbonates **2a** [14], **2b** [14], **2d** [14] and **2e** [14] were known compounds and have spectral data in accord with the reported ones.

*3.2. 4-Methyl-5-methylene-4-(1-methylethyl)-1,3-dioxolan-2-one **2c***

Colorless liquid. Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52: H, 7.75. Found: C, 59.98; H, 7.20. GC-MS: m/z 156(M^+, 0.1), 97(13), 70(100), 55(89), 43(63). IR(film): 1823, 1683 cm^{-1}. ^{1}H-NMR: δ 4.82 (1 H, d, $J = 3.8$, =CHH), 4.31 (1 H, d, $J = 3.8$, =CHH), 1.96 (1 H, m, CHMe$_2$), 1.585 and 1.586 (total 3 H, s each, –Me), 1.04 (3 H, d, $J = 6.7$, –*Me*Me), 1.01 (3 H, d, $J = 6.9$, –Me*Me*). ^{13}C-NMR: δ 157.1, 151.7, 89.9, 86.3, 37.0, 24.0, 16.3, 16.0.

*3.3. Preparation of α-alkylidene cyclic carbonate **2f** from **1f** and CO_2*

The propargylic alcohol **1f** (3 mmol) was agitated in the presence of K_2CO_3 (0.75 mmol) in DMAc (6 cm^3) under an atmospheric pressure of CO_2 (balloon) at 80°C for 5 h. Work-up in the same manner as above followed by column chromatography eluting with hexane–ethyl acetate(1:1) gave **2f** in 35% yield. (*Z*)-5-Benzylidene-4,4-dimethyl-1,3-dioxolan-2-one (*Z*)-**2f** Colorless solid. mp 38–41°C. Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.43; H. 5.94. GC-MS: m/z 204 (M^+, 11%), 160 (24), 145 (25), 132 (52), 117 (85), 91 (44), 69 (78), 44 (76), 41 (100). IR (KBr): 1820, 1700, 1050, 1010 cm^{-1}. ^{1}H-NMR: δ 7.56–7.23 (5 H, m, Ph), 5.50 (1 H, s, =CH), 1.69 (6 H, s, Me). ^{13}C-NMR: δ 151.3, 150.7, 132.4, 128.7, 128.4, 127.6, 101.6, 85.5, 27.7.

*3.4. Preparation of α-alkylidene cyclic carbonate **2g** from **1g** and CO_2*

The propargylic alcohol **1g** (2 mmol) was agitated in the presence of K_2CO_3 (0.5 mmol) in DMAc (4 cm^3) under an atmospheric pressure of CO_2 at 80°C for 5 h. Work-up in the same manner as above

followed by silica gel column chromatography eluting with hexane–ethyl acetate (20:1) gave **2g** in 15% yield.

3.5. (Z)-5-(But-2-ynylidene)-4-4-dimethyl-1,3-dioxolan-2-one [(Z)-**2g**]

Colorless solid. mp 98–101°C. Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H. 6.07. Found: C, 65.20; H, 6.29. GC-MS: *m / z* 166(M^+, 21), 122 (24), 94 (91), 79 (100), 44 (53), 41 (85). IR(KBr): 2223, 1837, 1686 cm^{-1}, ^{1}H-NMR: δ 4.75 (1H, quartet, $J = 2.4$, Me), 2.00 (3 H, d, $J = 2.4$, =CH), 1.60 (6 H, s, Me_2). ^{13}C-NMR: δ 160.0, 150.5, 92.8, 84.9, 83.3, 70.6, 27.5, 4.5.

3.6. Preparation of α-alkylidene cyclic carbonate **4a–d** from **1a**, CO_2, and alkyl halides

Propargylic alcohols **1a–c** (5 mmol) were allowed to react with alkyl halides at 100°C for 8 h in acetonitrile (10 cm^3) under the pressure of CO_2 (3 MPa) in the presence of $Pd(OAc)_2$ (0.1 mmol), PPh_3 (0.4 mmol) and K_2CO_3 (10 mmol). The product **4a–d** was isolated by silica gel chromatography or Kugel röhr distillation. Carbonate **4c** was a known compound and has spectral data in accord with the reported one [8].

3.7. (E)-Ethylidene-4,4-dimethyl-1,3-dioxolan-2-one [(E)-**4a**]

Colorless liquid. Anal. Calcd. for $C_7H_{10}O_3$:C, 59.14; H, 7.09. Found: C, 59.21; H, 7.05. GC-MS: *m / z* 142(M^+), 70, 55, 42; IR(film): 1830, 1720 cm^{-1}. ^{1}H-NMR: δ 5.22 (1 H, quartet, $J = 7.6$, =CH), 1.68 (6H, s, Me_2), 1.67 (3 H, d, $J = 7.6$, Me).

3.8. (E)-5-(But-3-enylidene)-4,4-dimethyl-1,3-dioxolan-2-one [(E)-**4b**]

Colorless liquid. Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27: H, 7.19. Found: C, 64.18; H, 7.21. GC-MS: *m / z* 168(M^+, 3), 109(14), 81(39), 70(82), 55(32), 42(100). IR(film): 3080, 1820, 1705, 1640, 1270, 1150 cm^{-1}. ^{1}H-NMR: δ 5.81 (1 H, ddt, $J = 17.4$, 10.0, 6.0, C*H*=CH_2), 5.23 (1 H, t, $J = 8.6$, =C*H*CH_2), 5.10 (1 H, ddt, $J = 17.4$, 1.4, 1.4, =CH_2), 5.09 (1 H, ddt, $J = 10.0$, 1.4, 1.4, =CH_2), 2.82–2.73 (2H, m, –CH_2–), 1.67 (6H, s, Me_2).

3.9. (Z)-5-(But-3-enylidene)-4,4-dimethyl-1,3-dioxolan-2-one [(Z)-**4b**]

Colorless liquid. Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.31; H, 7.26. GC-MS: *m / z* 168(M^+, 2), 124(8), 109(30), 81(24), 70(100), 42(90). IR(film): 3080, 1820, 1720, 1640, 1240, 1155 cm^{-1}. ^{1}H-NMR: δ 5.81 (1 H, ddt, $J = 16.4$, 10.0, 6.0, C*H*=CH_2), 5.07 (1 H, ddt, $J = 16.4$, 1.4, 1.4, =CH_2), 5.03 (1 H, ddt, $J = 10.0$, 1.4, 1.4, =CH_2), 4.63 (1 H, t, $J = 7.6$, =C*H*CH_2), 2.94–2.86 (2 H, m, –CH_2–), 1.59 (6 H, s, Me_2).

3.10. (E)-4,4-Dimethyl-5-(2-phenylethylidene)-1,3-dioxolan-2-one [(E)-**4d**]

Colorless liquid: GC-MS: *m / z* 218(M^+), 131, 119, 104, 91, 70, 42. IR(film): 3000, 1820, 1710, 1280, 1150, 1110 cm^{-1}. ^{1}H-NMR: δ 7.90–6.90 (5 H, m, Ph), 5.38 (1 H, t, $J = 8.4$, =CH), 3.39 (2H, d, $J = 8.4$, –CH_2–), 1.72 (6 H, s, Me_2).

3.11. Preparation of α-butenylidene cyclic carbonate **7a–c** from allylic propargylic carbonate **6a–c**

The allylic propargylic carbonate **6** (5 mmol), $Pd(dba)_2$ (0.1 mmol), $P(OPh_3)_3$ (0.4 mmol), KBr (0.5 mmol) and CH_3CN (10 cm^3) were charged in an autoclave, into which CO_2 was introduced up to 4 MPa. The autoclave was heated at 90°C for 5 h. After the reaction, the reaction mixture was taken up in diethyl ether (30 cm^3). The organic layer was separated and concentrated. The product **7** was isolated by silica gel column chromatography eluting with hexane–chloroform (1:1). Carbonate **7a** was a known compound and has spectral data in accord with the reported one [5].

3.12. (E)-5-(But-3-enylidene)-4-methyl-1,3-dioxolan-2-one [(E)-7b]

Colorless liquid. Anal. Calcd. for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.12; H, 6.72. GC-MS: *m / z* 154(M^+), 95, 67, 56, 39. IR(film): 3080, 1825, 1710, 1640, 1180, 1150 cm^{-1}. ^{1}H-NMR: δ 5.80 (1H, ddt, $J = 17.0, 10.0, 5.8$, C*H*=CH_2), 5.38–5.30 (1 H, m, C*H*Me), 5.30 (1H, td, $J = 8.3, 2.0$, –CH_2C*H*=), 5.09 (1 H, ddt, $J = 17.0, 1.5, 1.5$, =CH_2), 5.08 (1H, ddt, $J = 10.0, 1.5, 1.5$, =CH_2), 2.65–2.75 (2 H, m, –CH_2–), 1.56 (3H, d, $J = 6.4$, CH*Me*).

3.13. (E)-5-(But-3-enylidene)-1,3-dioxolan-2-one [(E)-7c]

Colorless liquid. GC-MS: *m / z* 140(M^+), 96, 68, 54, 39. IR(film): 3080, 1825, 1720, 1640, 1180, 1130 cm^{-1}. ^{1}H-NMR: δ 5.78 (1 H, ddt, $J = 17.0, 10.6, 6.0$, C*H*=CH_2), 5.38 (1H, tt, $J = 8.2, 2.7$, =C*H*CH_2), 5.08 (1H, ddt, $J = 17.0, 1.5, 1.5$, =CH_2), 5.07 (1H, ddt, $J = 10.6, 1.5, 1.5$, =CH_2), 5.01 (2H, dt, $J = 2.7, 1.4$, OCH_2), 2.70–2.61 (2H, m, –CH_2–).

3.14. (Z)-4,4-Dimethyl-5-(1-phenylbut-3-enylidene)-1,3-dioxolan-2-one [(Z)-7d]

Colorless solid. mp 68–72°C. Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.93; H, 6.60. GC-MS: m/z 244(M^+, 12), 200 (12), 129 (100), 115 (37), 77 (25). IR (KBr): 1800, 1690, 1640 cm^{-1}. ^{1}H-NMR: δ 7.23–7.38 (5H, m, Ph), 5.66 (1H, ddt, $J = 17.1, 10.3, 6.0$, CH=), 5.00–5.06 (2H, m, CH_2), 3.15 (2H, ddd, $J = 6.0, 1.6, 1.6$, –CH_2–), 1.78 (6H, s, Me_2). ^{13}C-NMR: δ 151.1, 146.9, 136.2, 134.3, 128.5, 128.2, 127.6, 117.3, 113.5, 84.9, 34.5, 27.0.

3.15. Preparation of allyl alcohol-D

Tetrahydropyranyl (THP) ether of propargyl alcohol was deuterated with *n*-BuLi and D_2O. The THP ether (50 mmol) was hydrogenated under an atmospheric pressure of H_2 with Lindlar catalyst (335 mg) in the presence of quinoline (211 mg) in pentane (10 cm^3) at an ambient temperature for 16 h. After the catalyst was filtered off, the reaction mixture was distilled at 67°C/2666 Pa to give the THP ether of the allyl alcohol-D in 76% yield. The stereochemistry around the double bond was determined by ^{1}H-NMR (*E:Z* = 14:86). The THP ether of the allyl alcohol-D (50 mmol) was subjected to the reaction with pyridinium *p*-toluenesulfonate (PPTS) (1 mmol) in octanol (50 cm^3) at 100°C for 2 h. The reaction mixture was distilled at 72°C/53,000 Pa to give the allyl alcohol-D in 55% yield.

*3.16. Preparation of allyl propargyl carbonate-D (**6c**-D)*

The allyl alcohol-D (30 mmol) and propargyl bromide (30 mmol) were agitated under an atmospheric pressure of CO_2 (balloon) in the presence of K_2CO_3 (60 mmol) in DMAc (90 cm^3) at 80°C for 4 h [21,22]. After the reaction, the mixture was taken up in diethyl ether and the inorganic salts were filtered off. The organic layer was washed with 0.5 M HCl solution, dried over $MgSO_4$, concentrated and distilled at 90°C/400 Pa to give 6c-D in 45% yield.

*3.17. Cyclization of allyl propargyl carbonate-D (**6c**-D)*

The reaction was performed in the similar manner as above using the allyl propargyl carbonate-D (**6c**-D: 5 mmol) as the substrate. The product was obtained by distillation under reduced pressure (120°C/133 Pa) in 12% yield. The ^{1}H-NMR spectrum indicated that the deuterium content of the C2 and C4 methylene groups in the butenylidene group were 42 and 30%, respectively.

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