Silver(I)-Promoted Cascade Reaction of Propargylic Alcohols, Carbon Dioxide, and Vicinal Diols: Thermodynamically Favorable Route to Cyclic Carbonates

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ABSTRACT: A silver(I)-promoted cascade reaction was developed for the synthesis of cyclic carbonates from terminal propargylic alcohols, carbon dioxide, and vicinal diols. Compared with direct condensation of vicinal diols with CO2, this protocol provides a thermodynamically favorable route to cyclic carbonates and α-hydroxyl ketones in excellent yields (up to 97%) without the additional dehydration step. Such a cascade procedure proceeds presumably through initial reaction of propargylic alcohol with CO2 and subsequent nucleophilic attack of vicinal alcohol on in situ-formed α-alkylidene cyclic carbonate, resulting in successive generation of α-alkylidene cyclic carbonate, unsymmetrical β-oxoalkyl carbonate, cyclic carbonate, and α-hydroxyl ketone.

INTRODUCTION

Carbon dioxide, as an abundant, readily available, nontoxic, and nonflammable carbon resource, is becoming a powerful synthon and useful C1 building block for the preparation of value-added chemicals.1 Cyclic carbonates, as one of the products from CO2 chemistry, are a class of heterocycles with a wide range of applications, being commonly used as polar aprotic solvents, electrolytes in batteries, monomers in the synthesis of polycarbonates, and reaction intermediates in the manufacture of fine chemicals.2 To date, numerous effective processes have been reported to prepare various cyclic carbonates from readily available CO2 as an alternative feedstock to carbon monoxide and phosgene, such as cycloaddition of epoxides with CO2,3 direct condensation of vicinal diols and CO2,4 and so on. Among these methodologies, cycloaddition of epoxides and CO2 with 100% atom economy has been extensively investigated, and a large number of catalysts have been reported so far.5,6 However, particular operation is required, owing to the toxicity and reactivity associated with use of epoxides.7

On the other hand, direct condensation of vicinal diols with CO2 can be considered as an alternative access to cyclic carbonates because 1,2-diols can be manufactured from biomass8 and water is the only by-product9 (Scheme 1a). In this respect, the established protocols with a variety of metal-based catalysts, such as Ce,10 Sn,11 Ge,12 Mg,13 and so forth, have been reported. However, the conversion of vicinal diols and yields of cyclic carbonates were unsatisfactory in most instances (e.g., 3.8% propylene carbonate yield with a Mg catalyst), even under harsh reaction conditions (generally >150 °C, 10 MPa), because of the thermodynamic limitation14 and/or inactivation of the catalysts by the water formed as a co-product during the reaction. Therefore, removal of water is crucial for overcoming the equilibrium limitation, and methodologies using nitrile15−17 as a dehydrating agent have been employed to shift the equilibrium to favor the formation of cyclic carbonate. Despite the considerable progress that has been seen, exploring efficacious catalytic approaches for the production of cyclic carbonates directly, starting from vicinal diols and CO2, could be still highly desirable and worthwhile.

In recent years, reactions of propargylic alcohols with CO2 have been well developed, to prepare organic carbonates,18 carbamates,19 oxazolidinones,20 3(2H)-furanones,21 and α-hydroxyl ketones.22 These preparative procedures likely proceed through a reaction sequence involving carboxylative cyclization of propargylic alcohols with CO2, subsequent attack of the nucleophile with in situ-generated α-alkylidene cyclic carbonate, resulting in α-alkylidene cyclic carbonate, unsymmetrical β-oxoalkyl carbonate, cyclic carbonate, and α-hydroxyl ketone.
ketone simultaneously. As such, dehydration can be avoided and the thermodynamically limited synthesis of cyclic carbonates from direct condensation of vicinal diols with CO₂ and formation of α-hydroxy ketones from propargylic alcohols are well cooperated in a thermodynamically favored manner \([\text{Scheme 1c, } \Delta_rG^{298.15 K} = -40.6 \text{ kcal mol}^{-1}, \text{ Table S2}]\). Herein, we would like to report an alternative strategy to concurrently afford cyclic carbonates and α-hydroxyl ketones from propargylic alcohols, CO₂, and vicinal diols via a three-component one-pot strategy.

**RESULTS AND DISCUSSION**

α-Alkylidene cyclic carbonate has been proven to be the vital intermediate in the cascade reaction of propargylic alcohol, CO₂, and an alcoholic nucleophile.²³,⁷b,d,¹²α On the other hand, silver compounds have been found to be efficient in catalyzing the carboxylative cyclization of propargylic alcohols with CO₂ to prepare α-alkylidene cyclic carbonates.⁴a,b,f,h,i Therefore, we initially explored the silver-promoted reaction of propane-1,2-diol (1a) and α-alkylidene cyclic carbonate IM-1 to validate our hypothesis. As shown in Table 1, no expected product was detected, with full recovery of 1a and IM-1, without any catalyst (entry 1). Gratifyingly, propylene carbonate (3a) and 3-hydroxy-3-methylbutan-2-one (α-hydroxyl ketone 4a) were obtained in the presence of Ag₂CO₃ (entry 2). Although triphenyl phosphine itself was found to be inactive under the given conditions (entry 3), addition of PPh₃ greatly enhanced the catalytic efficiency (entry 4 vs 2).

Subsequently, a series of silver compounds were screened, in combination with PPh₃ (entries 5–11). Silver compounds, such as Ag₂CO₃, Ag₂WO₄, Ag₃PO₄, and Ag₂O showed promising activity (entries 5–8). However, AgCl, AgI, and AgNO₃ did not work at all (entries 9–11).

Encouraged by the results, the three-component reaction of propargylic alcohol 2a, CO₂, and vicinal diol 1a was selected as a model reaction to further investigate the one-pot synthesis of cyclic carbonate 3a, with the coproduction of α-hydroxyl ketone 4a. As summarized in Table 2, no reaction occurred without a catalyst (entry 1). Then, several representative silver compounds as π-Lewis acidic species were primarily screened in conjunction with PPh₃ (entries 2–7). Silver compounds, such as Ag₂CO₃, Ag₂O, AgOAc, and Ag₂WO₄, effectively promoted the three-component cascade reaction, with the assistance of PPh₃ to afford cyclic carbonate 3a and α-hydroxyl ketone 4a in moderate yield (entries 2–5). However, AgNO₃ and AgBF₄ displayed no activity (entries 6 and 7). These results suggest the role of alkalinity of the silver catalyst. Furthermore, both

| Table 1. Reaction of 1,2-Diol with α-Alkylidene Cyclic Carbonate<sup>a</sup> |
|-----------------|-----------------|-----------------|-----------------|
| entry | catalyst | ligand/additive | 3a yield (%)<sup>b</sup> | 4a yield (%)<sup>b</sup> |
| 1 | 0 | 0 | 0 |
| 2 | Ag₂CO₃ | 20 | 20 |
| 3 | PPh₃ | 0 | 0 |
| 4 | Ag₂CO₃ | PPh₃ | 77(93)<sup>c</sup> | 79(91)<sup>c</sup> |
| 5 | AgOAc | PPh₃ | 68 | 70 |
| 6 | Ag₂WO₄ | PPh₃ | 79 | 80 |
| 7 | Ag₃PO₄ | PPh₃ | 81 | 82 |
| 8 | Ag₂O | PPh₃ | 81 | 83 |
| 9 | AgCl | PPh₃ | 0 | 0 |
| 10 | AgI | PPh₃ | 0 | 0 |
| 11 | AgNO₃ | PPh₃ | 0 | 0 |

<sup>a</sup>Reaction conditions: 1a, 152.2 mg, 2 mmol; IM-1, 256.2 mg, 2 mmol; catalyst, 0.1 mmol, 5 mol %; ligand/additive, 0.2 mmol, 10 mol %; CH₃CN, 2 mL; 80 °C; 4 h. <sup>b</sup>Gas chromatography (GC) yield. <sup>c</sup>12 h.
Ag₂CO₃ and PPh₃ alone were found to be ineffective (entries 8 and 9), hinting that [(PPh₃)₂Ag]₂CO₃ may be the active species. Various mono- and bi-dentate phosphines (L₂−L₇) were examined (entries 10−16). All phosphines selected as ligands gave the desired products in good yields, and electron-rich bidentate phosphine L₆, with a large bite angle, exhibited the highest efficiency, affording 3a and 4a in excellent yields (entry 15). Excellent results could also be obtained on reducing the CO₂ pressure to 1.0 MPa (entry 17), whereas further decrease in the pressure to 1 bar gave poor results (entry 18). Therefore, a suitable reaction pressure could be 1.0 MPa.

With the establishment of suitable reaction conditions, the generality of this three-component reaction was explored, as listed in Table 3. In the presence of 5 mol % of Ag₂CO₃ and 10 mol % of L₆ under a 1.0 MPa CO₂ atmosphere at 80 °C, symmetrical ethylene glycol 1b gave ethylene carbonate 3b in 84% yield and 4a in 89% yield (entry 2). Meanwhile, methyl-, ethyl-, n-propyl-, phenyl-, and phenoxyalkyl-substituted unsymmetrical vicinal diols 1a, 1c, 1d, 1e, and 1f were efficiently converted into the corresponding cyclic carbonates 3a, 3c, 3d, 3e, and 3f, respectively (entries 1 and 3–6).

Glycerol carbonate, a kind of heterocyclic compound, is commonly used in polymer synthesis. Ideally, it is prepared through the carboxylation of glycerol with CO₂, which represents a sustainable process that is able to convert two cheap materials into a valuable chemical, with water as the by-product. However, a high pressure is usually required. However, the productivity is low, probably owing to the thermodynamic limitation. In this work, this obstacle could be surmounted through the design of a protocol to concurrently obtain two value-added products with 100% atom economy; thus, glycerol carbonate could be obtained by employing the Ag(I)-promoted cascade reaction of terminal propargylic alcohols, CO₂, and vicinal diols in a one-pot process. For example, 3g was obtained in 80% yield together with 4a in 91% yield (entry 7). To our delight, a high yield of 3g was also acquired in a "gram-scale" experiment (Scheme 2). Accordingly, this protocol also offers an alternative route to the production of glycerol carbonate from glycerol and CO₂. Moreover, several other alkyl- and phenyl-substituted propargylic alcohols (2b–e) also afforded the desired cyclic carbonate, 3a, successfully and α-hydroxyl ketones 4b–e concomitantly (entries 11–14).

![Table 2. Three-Component Reaction of Propargylic Alcohol, CO₂, and Vicinal Diol]

| entry | catalyst | ligand/additive | 3a yield (%)<sup>b</sup> | 4a yield (%)<sup>b</sup> |
|-------|----------|----------------|--------------------------|--------------------------|
| 1     | Ag₂CO₃   | PPh₃           | 0                        | 0                        |
| 2     | Ag₂CO₃   | L₁             | 83                       | 82                       |
| 3     | Ag₂CO₃   | L₂             | 88                       | 92                       |
| 4     | Ag₂CO₃   | L₃             | 75                       | 78                       |
| 5     | Ag₂CO₃   | L₄             | 73                       | 73                       |
| 6     | Ag₂CO₃   | L₅             | 74                       | 76                       |
| 7     | Ag₂CO₃   | L₆             | 93 (87)<sup>c</sup>      | 91                       |
| 8     | Ag₂CO₃   | L₇             | 82                       | 82                       |
| 9     | PPh₃     | L₂             | 0                        | 0                        |
| 10    | Ag₂CO₃   | L₁             | 92                       | 92                       |
| 11    | Ag₂CO₃   | L₆             | 59                       | 57                       |
| 12    | Ag₂CO₃   | L₇             | 82                       | 82                       |
| 13    | Ag₂CO₃   | L₆             | 92                       | 92                       |
| 14    | Ag₂CO₃   | L₆             | 59                       | 57                       |

<sup>a</sup>Reaction conditions: 1a, 152.2 mg, 2 mmol; 2a, 168.2 mg, 2 mmol; CO₂, 2 MPa; catalyst, 0.1 mmol, 5 mol %; ligand/additive, 0.2 mmol, 10 mol %; CH₃CN, 2 mL; 80 °C; 12 h. <sup>b</sup>GC yield. <sup>c</sup>Isolated yield. <sup>d</sup>CO₂, 1.0 MPa. <sup>e</sup>CO₂, 1.0 bar.
Notably, the configuration of 4e, with the retention of stereochemistry, was unambiguously confirmed by single-crystal X-ray analysis (Supporting Information). Interestingly, this protocol was also applied to the synthesis of sterically congested cyclic carbonates such as 3h and 3i (entries 8 and 9) and the six-membered cyclic carbonate, 3j (entry 10).

To verify the reaction pathway, several control experiments were conducted, as described in Scheme 3. As expected, the
reaction of 2-methylbut-3-yn-2-ol 2a with CO$_2$ in the absence of propane-1,2-diol (1a) gave α-alkylidene cyclic carbonate IM-1 (Scheme 3a).

Moreover, 1a did not react with CO$_2$ under the given conditions (Scheme 3b), indicating that direct condensation of 1,2-diol with CO$_2$ in the presence of a silver catalyst did not happen at all. However, α-alkylidene cyclic carbonate IM-1 well reacted with 1a, affording the targeted cyclic carbonate, 3a, along with the simultaneous formation α-hydroxyl ketone 4a as a co-product smoothly (Scheme 3c). Accordingly, the α-alkylidene cyclic carbonate was confirmed as the carbonyl source.

Furthermore, labeling experiments were also carried out to further understand the reaction mechanism. When 1a reacted with the $^{13}$C-labeled α-alkylidene cyclic carbonate, IM-1′, from $^{13}$CO$_2$, a $^{13}$C$_{carboxy}$-labeled cyclic carbonate (3a′) was obtained smoothly (Scheme 3d). Meanwhile, the treatment of deuterated phenyl-substituted 1,2-diol (3e′) with α-alkylidene cyclic carbonate IM-2 gave the deuterated α-hydroxyl ketone (Scheme 3e). These results demonstrated that the α-alkylidene cyclic carbonate from CO$_2$ is the unique carbonyl source and...
the protons of the vicinal diol are eventually incorporated into the α-hydroxyl ketone.

On the basis of the above-described results and previous reports,3,7−12 we proposed a reaction pathway as depicted in Scheme 4. The α-alkylidene cyclic carbonate intermediate is first generated through the reaction of propargylic alcohol 2 with CO2,3,7−12 which then undergoes a nucleophilic ring-opening reaction by vicinal diol to generate the corresponding hydroxyl-substituted unsymmetrical carbonate, A. The silver catalyst presumably activates the hydroxyl of intermediate A thereby resulting in an intramolecular nucleophilic cyclization to afford cyclic carbonate 3 and α-hydroxy ketone 4 concurrently.

■ CONCLUSIONS

In summary, we have developed an efficient silver(I)-promoted three-component protocol comprising terminal propargylic alcohols, carbon dioxide, and vicinal diols for expeditious utilization of CO2 to concurrently prepare cyclic carbonates from vicinal diols and CO2 in a thermodynamically favorable manner, along with the formation of α-hydroxy ketones. This is a versatile “one-pot” approach to prepare valuable products, and CO2 is used as both a carbonyl and oxygen source to form C=O and C=O bonds simultaneously. Notably, the unfavorable thermodynamic equilibrium in the condensation reaction of vicinal diols with CO2 is not involved when using this cascade three-component strategy to cyclic carbonates, with no need for a dehydration process.

■ EXPERIMENTAL SECTION

Materials. Unless otherwise noted, all starting materials were obtained from TCI, Aladdin, or Alfa Aesar and used as received. Carbon dioxide (99.99% purity) was commercially available.

Analytical Methods. 1H NMR spectra were recorded on 400 MHz spectrometers using CDCl3 or DMSO-d6 as the solvent, referenced to CDCl3 (7.26 ppm) or DMSO-d6 (2.50 ppm). 13C NMR was recorded at 100.6 MHz in CDCl3 (77.00 ppm) or DMSO-d6 (39.52 ppm). Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet, and broad signal. High-resolution mass spectrometry (MS) was conducted using a Varian 7.0 T Fourier transform ion cyclotron resonance—MS by the electrospray ionization (ESI) technique. GC analyses were carried out using Shimadzu GC-2014, equipped with a flame-ionization detector and a capillary column (RTX-50, 30 μm × 25 μm). Mass spectra were recorded using Shimadzu GCMS-QP2010, with an RTX-SMS capillary column, at an ionization voltage of 70 eV. The data are given as mass units per charge (m/z).

General Procedure for the Reaction of 1,2-Diol with α-Alkylidene Cyclic Carbonate. The catalyst (0.1 mmol, 5 mol %), ligand/additive (0.2 mmol, 10 mol %), 1a (152.2 mg, 2 mmol), IM-1 (256.2 mg, 2 mmol), L6 (115.7 mg, 10 mol %), 2-methylbut-3-yn-2-ol (168.2 mg, 2 mmol), and CH3CN (2.0 mL) were added to a 10 mL Schlenk tube containing a stirrer bar. Next, the Schlenk tube was sealed and connected with a CO2 balloon. The reaction mixture was stirred at 25 °C. After the reaction had completed, excessive CO2 was carefully released. The mixture was transferred to a round-bottomed flask and flushed with 3 × 20 mL of Et2O. Solvents were removed under vacuum, and the residue was purified by silica gel column chromatography using petroleum ether/ethanol acetate as an eluent to give IM-1 in 97% yield.

General Procedure for the Cascade Reaction of Propargylic Alcohols, CO2, and Vicinal Diols. The reactions were performed in a 25 mL autoclave with a glass vessel inside. Ag2CO3 (27.6 mg, 0.1 mmol), L6 (115.7 mg, 0.2 mmol), propargylic alcohol (2.0 mmol), vicinal diol (2.0 mmol), and CH3CN (2.0 mL) were successively added. The autoclave was sealed and filled with carbon dioxide. Then, the reaction mixture was allowed to stir at 80 °C for a desired time. After the reaction had completed, the vessel was cooled in an ice-bath and excessive CO2 was carefully released. The mixture was transferred to a round-bottomed flask and flushed with 3 × 5 mL of CH2Cl2. Solvents were removed under vacuum, and the residue was purified by silica gel column chromatography using petroleum ether/ethanol acetate as an eluent to give the desired products, 3 (10/1−5/3) and 4 (50/1−20/1).

Procedure for “Gram-Scale” Reaction. The reaction was performed in a 50 mL autoclave with a glass vessel inside. Ag2CO3 (0.1654 g, 5 mol %), L6 (0.6943 g, 10 mol %), 2-methylbut-3-yn-2-ol (1.0092 g, 12 mmol), glycerol (1.0152 g, 12 mmol), and CH3CN (6 mL) were successively added. Then, the autoclave was sealed and filled with carbon dioxide. The reaction mixture was allowed to stir at 80 °C for 16 h. After the reaction had completed, the vessel was cooled in an ice-bath and excessive CO2 was carefully released. The yields of the products were determined by 1H NMR with 1,1,2,2-tetrachloroethane in CDCl3 as the internal standard.

Reaction Mechanism Investigation. Procedure for the Synthesis of IM-1. The reactions were performed in a 25 mL autoclave with a glass vessel inside. Ag2CO3 (27.6 mg, 5 mol %), L6 (115.7 mg, 10 mol %), 2-methylbut-3-yn-2-ol (168.2 mg, 2 mmol), and CH3CN (2.0 mL) were successively added. Then, the autoclave was sealed and filled with carbon dioxide. The reaction mixture was allowed to stir at 80 °C for 12 h. After the reaction had completed, the vessel was cooled in an ice-bath and excessive CO2 was carefully released. The yield of IM-1 was determined by 1H NMR with 1,1,2,2-tetrachloroethane in CDCl3 as the internal standard (Scheme 3a).

Procedure for the Synthesis of 4-Methyl-1,3-dioxolan-2-one (3a). The reactions were performed in a 25 mL autoclave with a glass vessel inside. Ag2CO3 (27.6 mg, 5 mol %), L6 (115.7 mg, 10 mol %), propane-1,2-diol (152.2 mg, 2 mmol), and CH3CN (2.0 mL) were successively added. Then, the autoclave was sealed and filled with carbon dioxide. The reaction mixture was allowed to stir at 80 °C for 12 h. After the reaction had completed, the vessel was cooled in an ice-bath and excessive CO2 was carefully released. The yield of product 3a was determined by 1H NMR with 1,1,2,2-tetrachloroethane in CDCl3 as the internal standard (Scheme 3b).

Procedure for the Synthesis of 3a and 3-Hydroxy-3-methylbutan-2-one (4a). Ag2CO3 (27.6 mg, 5 mol %), L6 (115.7 mg, 10 mol %), 1a (152.2 mg, 2 mmol), IM-1 (256.2 mg, 2 mmol), and CH3CN (2 mL) were added to a 10 mL Schlenk tube containing a stirrer bar. Next, the Schlenk tube was connected to a nitrogen line with a bubbler and stirred at
80 °C for 24 h. When the reaction had completed, the Schlenk tube was cooled to room temperature. Biphenyl was added as an internal standard, and the mixture was filtered through a short silica column. Then, the filtrate was submitted to analysis of the yield of 3a and 4a by GC (Scheme 3c).

**Procedure for the Synthesis of 13Ccarbonyl-Methyl-1,3-dioxolan-2-one (IM-1).** A 10 mL Schlenk tube equipped with a stirrer bar was charged with Ag2CO3 (13.8 mg, 15 mol %), PPh3 (26.2 mg, 10 mol %), and Et3N (0.0125 mmol). The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give IM-1 in 92% yield (Scheme 3d).

**Procedure for the Synthesis of 13Ccarbonyl-4-Methyl-1,3-dioxolan-2-one (3a) and 4a.** A 10 mL Schlenk tube equipped with a stirrer bar was charged with Ag2CO3 (13.8 mg, 5 mol %), PPh3 (26.2 mg, 10 mol %), 1a (76.1 mg, 1 mmol), IM-1 (128.1 mg, 1 mmol), and CH2CN (1 mL). Next, the Schlenk tube was sealed to a nitrogen line with a bubbler and heated at 80 °C for 12 h. When the reaction had completed, the Schlenk tube was cooled to room temperature. The yield of 4a was determined by1H NMR, with 1,1,2,2-tetrachloroethane in CDCl3 as the internal standard. Then, the reaction mixture was flushed with 3 × 5 mL CH2Cl2 and removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give 3a.

**Procedure for the Synthesis of 4-Methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one (IM-2).** A 10 mL Schlenk tube equipped with a stirrer bar was charged with Ag2CO3 (3.5 mg, 1 mmol), PPh3 (13.1 mg, 0.05 mmol), and C6H5CH3 (0.0125 mmol). The reaction mixture was stirred at 25 °C for 18 h. Carefully releasing excess CO2, the mixture was flushed with 3 × 5 mL Et2O and removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give IM-2 in 96% yield (Scheme 3e).

**Procedure for the Synthesis of 4-Phenyl-1,3-dioxolan-2-one (3e) and 3-Hydroxy-3-phenyl-1-deuteriobutan-2-one (4d).** A 10 mL Schlenk tube equipped with a stirrer bar was charged with Ag2CO3 (13.8 mg, 5 mol %), PPh3 (26.2 mg, 10 mol %), 3e (140.2 mg, 1 mmol), and CD2Cl2 (1 mL). Next, the Schlenk tube was sealed to a nitrogen line with a bubbler and heated at 80 °C for 18 h. When the reaction had completed, the Schlenk tube was cooled to room temperature. The residue was flushed with 3 × 5 mL of CH2Cl2 and removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give 3e and 4d.

**Characterization Data.** 4-Methyl-1,3-dioxolan-2-one (3a). Colorless liquid, 2 mmol scale, yield 177.6 mg, 87%. 1H NMR (400 MHz, CDCl3): δ 4.88–4.80 (m, 1H), 4.56–4.52 (t, J = 8.0 Hz, 1H), 4.03–3.99 (t, J = 7.8 Hz, 1H), 1.48–1.46 (d, J = 6.2 Hz, 3H) ppm. 13C NMR (100.6 MHz, CDCl3): δ 155.0, 73.5, 70.6, 19.4 ppm. HRMS (ESI): C8H11O3 [M + H]+ calced 130.0580, found: 130.0578.

4-Ethyl-1,3-dioxolan-2-one (3c). Yellow liquid, 2 mmol scale, yield 206.7 mg, 89%. 1H NMR (400 MHz, CDCl3): δ 4.71–4.61 (m, 1H), 4.52 (t, J = 8.1 Hz, 1H), 4.08 (dd, J = 8.4, 7.0 Hz, 1H), 1.88–1.67 (m, 2H), 1.02 (t, J = 7.5 Hz, 3H) ppm. 13C NMR (100.6 MHz, CDCl3): δ 155.5 (C=O), 64.6 ppm. GC–MS (EI, 70 eV) m/z (%) 89 (4), 88 (100), 73 (3).

4-Propyl-1,3-dioxolan-2-one (3d). Yellow liquid, 2 mmol scale, yield 169.2 mg, 65%. 1H NMR (400 MHz, CDCl3): δ 4.75–4.65 (m, 1H), 4.51 (t, J = 8.1 Hz, 1H), 4.05 (t, J = 7.8 Hz, 1H), 1.78 (ddd, J = 17.6, 11.6, 7.6 Hz, 1H), 1.69–1.58 (m, 1H), 1.57–1.33 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm. 13C NMR (100.6 MHz, CDCl3): δ 155.1, 76.7, 69.3, 35.8, 17.7, 13.6 ppm. GC–MS (EI, 70 eV) m/z (%) 131 (100), 43 (55), 69 (85), 39 (44), 41 (33), 86 (14), 57 (13), 85 (11).

4-Phenyl-1,3-dioxolan-2-one (3e). Yellow liquid, 2 mmol scale, yield 298.8 mg, 91%. 1H NMR (400 MHz, CDCl3): δ 7.49–7.33 (m, 5H), 6.66 (t, J = 8.0 Hz, 1H), 4.78 (t, J = 8.4 Hz, 1H), 4.31 (t, J = 8.2 Hz, 1H) ppm. 13C NMR (100.6 MHz, CDCl3): δ 154.8, 135.7, 129.7, 129.2, 125.8, 77.9, 77.1 ppm. GC–MS (EI, 70 eV) m/z (%) 164 (69), 91 (96), 90 (100), 78 (78).

4-(Phenoxy)methyl-1,3-dioxolan-2-one (3f). White solid, mp 99–100 °C, 2 mmol scale, yield 345.6 mg, 89%. 1H NMR (400 MHz, CDCl3): δ 7.31 (dd, J = 8.5, 7.5 Hz, 2H), 7.03 (d, J = 7.4 Hz, 1H), 6.92 (d, J = 7.9 Hz, 2H), 5.07–4.98 (m, 1H), 4.62 (t, J = 8.4 Hz, 1H), 4.54 (dd, J = 8.5, 5.9 Hz, 1H), 4.24 ppm.
Yellow liquid, 2 mmol scale, yield 147.8 mg, 52%. ¹H NMR (400 MHz, CDCl₃): δ 4.68 (s, 2H), 1.89 (d, J = 5.1 Hz, 1H), 1.36 (d, J = 8.0 Hz, 1H), 1.35 (s, 3H), 1.06 (s, J = 6.8, 2H), 0.74 (s, 3H). ¹³C NMR (100.6 MHz, CDCl₃): δ 149.1, 91.3, 78.1, 31.9, 29.4, 22.4, 16.1, 18.1 ppm. GC–MS (EI, 70 eV) m/z (%): 71 (100), 69 (24), 83 (20), 86 (20), 68 (19), 67 (17), 95 (10), 70 (10), 97 (10).

3-Hydroxy-3-methylbutan-2-one (4a). Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 5.24 (s, 1H), 2.15 (s, 3H), 1.17 (s, 6H) ppm. ¹³C NMR (100.6 MHz, DMSO-d₆): δ 134.9, 67.5, 31.2, 28.2, 26.3, 22.7 ppm. GC–MS (EI, 70 eV) m/z (%): 102 (9), 87 (100), 69 (62), 60 (92).

3-Hydroxy-3-methylpentan-2-one (4b). Colorless oil. ¹H NMR (400 MHz, DMSO-d₆): δ 5.04 (OH, 1H), 2.13 (s, 3H), 1.64–1.42 (m, 2H), 1.12 (s, 3H), 0.74 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (100.6 MHz, DMSO-d₆): δ 214.2, 78.6, 31.8, 25.1, 24.1, 7.9 ppm. GC–MS (EI, 70 eV) m/z (%): 43 (100), 73 (25), 87 (21), 45 (17), 57 (12), 101 (10).

1-(1-Hydroxycyclohexyl)ethanone (4c). Yellow oil, 2 mmol scale, yield 241.7 mg. ¹H NMR (400 MHz, CDCl₃): δ 2.24 (s, 3H), 1.75–1.64 (m, 6H), 1.49 (d, J = 6.5 Hz, 2H), 1.28 (dd, J = 15.1, 10.3 Hz, 2H) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ 212.7, 78.0, 33.8, 25.3, 23.7, 21.1 ppm. GC–MS (EI, 70 eV) m/z (%): 99 (71), 81 (100), 79 (21).

3-Hydroxy-3-phenylbutan-2-one (4d). Brown oil, 2 mmol scale, yield 218.5 mg, 87%. ¹H NMR (400 MHz, DMSO-d₆): δ 7.43 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.1 Hz, 1H), 6.06 (s, 1H), 2.02 (s, 3H), 1.52 (s, 3H) ppm. ¹³C NMR (100.6 MHz, DMSO-d₆): δ 210.0, 143.0, 127.9, 126.9, 124.7, 79.4, 25.8, 24.0 ppm. GC–MS (EI, 70 eV) m/z (%): 121 (100), 105 (19), 77 (31).

17-Hydroxy-17βHpregn-4-ene-3,20-dione (4e). White solid, mp 192–193 °C. ¹H NMR (400 MHz, CDCl₃): δ 5.69 (1H), 2.96 (1H), 2.38–2.27 (5H), 2.23 (3H), 1.98–1.95 (1H), 1.86–1.83 (1H), 1.74–1.36 (10H), 1.16 (3H), 1.06–1.02 (1H), 0.95 (3H), 0.90–0.82 (1H). ¹³C NMR (100.6 MHz, CDCl₃): δ 214.2, 199.4, 171.0, 123.8, 90.7, 53.2, 49.1, 47.5, 38.5, 36.1, 35.6, 35.0, 33.8, 33.0, 32.7, 31.5, 28.2, 24.2, 20.7, 17.3, 14.1 ppm. HRMS (ESI): C₂₉H₄₃O₅ for [M + H]+ calcd: 331.2268, found: 331.2274.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00407.

Crystallography of α-hydroxyl ketone 4e (CIF)

DFT calculations, NMR spectra of products (PDF)

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**Notes**

The authors declare no competing financial interest.

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**ADDITIONAL NOTES**

Thermodynamically unfavored reaction: ΔH (298.15 K, in vacuo) = 7.9 kcal/mol, ΔG (298.15 K, in vacuo) = 8.8 kcal/mol. For the detailed calculation, see the Supporting Information (Table S1).

**CCDC 1470569 (4e)** contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

**α-Hydroxyl ketone 4d** was finally isolated, presumably due to the further H/D exchange upon column chromatography.

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