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View Article Online
DOI: 10.1039/C8CC03039A

COMMUNICATION

# Synthesis of tetronic acids from propargylic alcohols and $CO_2$

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Received 00th January 20xx,
Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x

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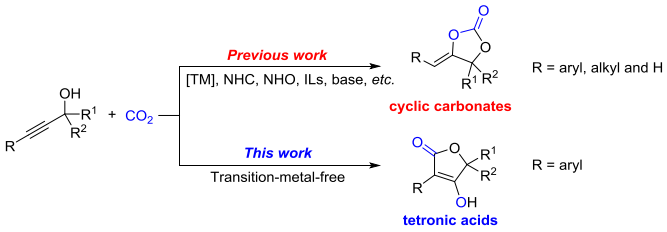
**A direct and practical synthesis of important tetronic acids from easily-available propargylic alcohols and carbon dioxide is reported for the first time. This transition-metal-free transformation features high atom- and step-economy, mild reaction conditions, good functional group tolerance and high yield. Preliminary mechanistic studies suggest that the reaction proceeds via cyclization to give alkylidene cyclic carbonate, ring-opening and re-cyclization processes.**

Carbon dioxide ($CO_2$), well-known as the greenhouse gas, is also an important C1 synthon in organic synthesis owing to its abundance, easy availability, and low toxicity. Although the thermodynamic stability and kinetic inertness make it difficult to be utilized efficiently, various kinds of selective organic transformations of $CO_2$ have been achieved in recent years.[1] Among them, numerous effort has been devoted to the synthesis of alkylidene cyclic carbonates from propargylic alcohols with $CO_2$ (Scheme 1).[1i,1l,2] Diverse catalysts, such as silver,[3] zinc,[4] copper,[5] palladium,[6] cobalt,[7] ruthenium,[8] phosphine,[9] *N*-heterocyclic carbene (NHC),[10] *N*-heterocyclic olefin (NHO),[11] ionic liquids (ILs),[12] and base,[13] have been proven to significantly promote this transformation. In contrast, the straightforward transformations to other high-value-added chemicals from propargylic alcohols with $CO_2$ are less developed. For example, Yamada and co-workers reported the elegant Ag-catalyzed rearrangement of propargylic alcohols to form α,β-unsaturated ketones containing the oxygen from $CO_2$.[14] Jiang, Qi, Yuan, Liu and Wang reported the novel $CO_2$-mediated hydration of propargylic alcohols to give α-hydroxyl ketones[15] or 3(2*H*)-furanones.[16] Although $CO_2$ is vital to these transformations,[15-16] it is not incorporated into these products. The generation of other important chemicals from propargylic alcohols with incorporation of $CO_2$ is highly appealing but challenging.




**Scheme 1** Incorporation of $CO_2$ into aryl propargylic alcohols

Tetronic acids are valuable intermediates and important motifs in agricultural, pharmaceutical, and biological chemistry.[17] Plenty of routes have been developed to prepare them.[18] However, many of them suffer from long synthetic routes, harsh reaction conditions or unstable starting materials. Thus, an alternative strategy to synthesize tetronic acids from simple and readily-available substrates in a sustainable process is highly desirable. As an ongoing endeavour to demonstrate the wide applications of $CO_2$ in organic synthesis,[19] we report a novel and practical method for the synthesis of tetronic acid derivatives from propargylic alcohols and $CO_2$ for the first time. This transition-metal-free process features mild reaction conditions, high atom- and step-economy, good functional group tolerance and high yield (Scheme 1).

When we tested the reaction of 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzonitrile **1a** with $CO_2$ in 1,3-dimethyl-2-imidazolidinone (DMI), we were unexpected to obtained the tetronic acid **2a** in 19% yield (Table 1, entry 1). The interest in this important tetronic acid drove us to further investigate the reaction conditions. Next, various kinds of bases (Table 1, entries 2-10) were screened. To our delight, the reaction proceeded smoothly in the presence of $Cs_2CO_3$ to give the desired product **2a** in 90% isolated yield (Table 1, entry 8). Subsequently, we also tested different solvents and found that DMI behaved better than other solvents (Table 1, entries 11-16). It is worth noting that shorter reaction time also led to high yield in this case, as the reaction also afforded **2a** in 86% yield in 2 hours (Table 1, entry 17). Although higher efficiency of this transformation with more equivalents of base was

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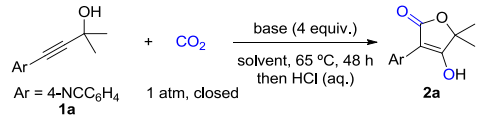
Electronic Supplementary Information (ESI) available: Experimental details and characterization data. See DOI: 10.1039/x0xx00000x

observed, the reaction with less amount of $Cs_2CO_3$ also provided **2a** in moderate to excellent yield (Table 1, entries 18 and 19). Notably, the inductively coupled plasma mass spectrometry (ICP-MS) test indicated that this reaction was a transition-metal-free process (please see ESI for more details).

**Table 1** Reaction conditions optimization[a]




| Entry | Base | Solvent | Yield (%) |
|---|---|---|---|
| 1 | DBU | DMI | 19 |
| 2 | MTBD | DMI | 31 |
| 3 | DABCO | DMI | 0 |
| 4 | TBD | DMI | 68 |
| 5 | $Li_2CO_3$ | DMI | N.D. |
| 6 | $Na_2CO_3$ | DMI | 4 |
| 7 | $K_2CO_3$ | DMI | 52 |
| **8** | **$Cs_2CO_3$** | **DMI** | **90 (90)** |
| 9 | CsF | DMI | 8 |
| 10 | CsOAc | DMI | 7 |
| 11 | $Cs_2CO_3$ | DMF | 38 |
| 12 | $Cs_2CO_3$ | DMA | 63 |
| 13 | $Cs_2CO_3$ | NMP | 71 |
| 14 | $Cs_2CO_3$ | DMSO | 51 |
| 15 | $Cs_2CO_3$ | MeCN | 38 |
| 16 | $Cs_2CO_3$ | THF | 9 |
| **17**[b] | **$Cs_2CO_3$** | **DMI** | **86** |
| 18[c] | $Cs_2CO_3$ | DMI | 55 |
| **19**[d] | **$Cs_2CO_3$** | **DMI** | **82** |

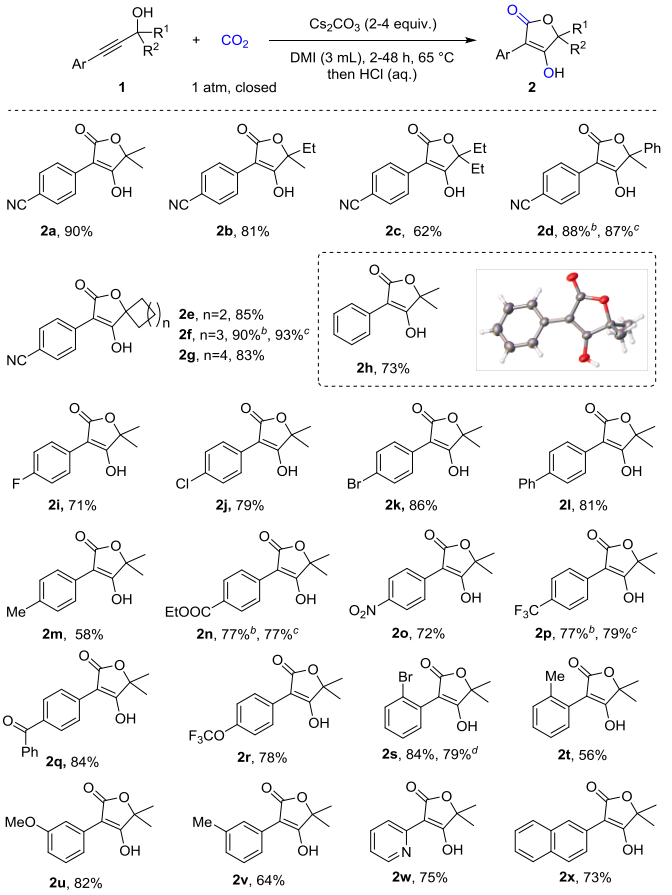
[a] Reaction conditions: **1a** (0.4 mmol), 1 atm of $CO_2$, base (4 equiv.), solvent (3 mL), 65 °C, 48 h. Determined by UPLC using benzophenone as internal standard. The yield in parentheses is isolated yield. [b] 2 h. [c] 1 equivalent of $Cs_2CO_3$ was used. [d] 2 equivalents of $Cs_2CO_3$ was used. N.D. = Not Detected. DMF = *N*,*N*-dimethylformamide. DMA = *N*,*N*-dimethylacetamide. NMP = *N*-methyl-2-pyrrolidone. DMSO = dimethyl sulfoxide. THF = tetrahydrofuran. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene. MTBD = 1,3,4,6,7,8-hexahydro-1-methyl-2H-pyrimido[1,2-α]pyrimidine. DABCO = 1,4-diazabicyclo[2.2.2]octane. TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

With the optimized reaction conditions in hand (Table 1, entry 8), we first investigated the substrates with different substituents at the α-position of hydroxyl group (Table 2). The substrates with both symmetric (**1a** and **1c**) and unsymmetric dialkyl groups (**1b**) could provide the desired products in good yields. The substrate **1d** with methyl and phenyl substitution also worked well to deliver the corresponding product **2d** in 87% yield. Moreover, the cyclic tertiary alcohols, including five- (**1e**), six- (**1f**), and seven-membered rings (**1g**), also afforded the tetronic acids **2e-g** with excellent yields.

Next, we tested the substrates with different substitutions on the arenes. We found that diverse aryl propargylic alcohols bearing electron-withdrawing groups (EWGs) or electron-donating groups (EDGs) could afford the desired products **2h-2x** in 56%-86% yields. It was obvious that substrates bearing EWGs showed higher reactivity than those with EDGs at the *para* position, which might benefit from the higher electrophilicity of the C–C triple bond toward in-situ generated carbonate anion. The structure of **2h** was confirmed by the X-ray crystal structure analysis.[20] Various kinds of functional groups, including fluoro (**2i**), chloro (**2j**), bromo (**2k** and **2s**), ester (**2n**), nitro (**2o**), trifluoromethyl (**2p**), ketone (**2q**), and methoxyl (**2u**), were well tolerated in this reaction, which provided huge opportunities for subsequent transformations. Besides *para*-substituents (**2i**-**2r**), the substrates with *ortho*-(**2s** and **2t**) or *meta*- (**2u** and **2v**) substitutions on the arenes were suitable to the reaction, providing desired products in moderate to good yields. To our delight, propargylic alcohols bearing pyridine (**2w**) or naphthalene (**2x**) could also react smoothly. Notably, a gram-scale synthesis of **2s** was carried out with the yield of 79% under the standard conditions, demonstrating the applicability of this method. Unfortunately, those substrates bearing alkyl or just hydrogen at 3-position of propargylic alcohols are not suitable for this reaction.

View Article Online DOI: 10.1039/C8CC03070H

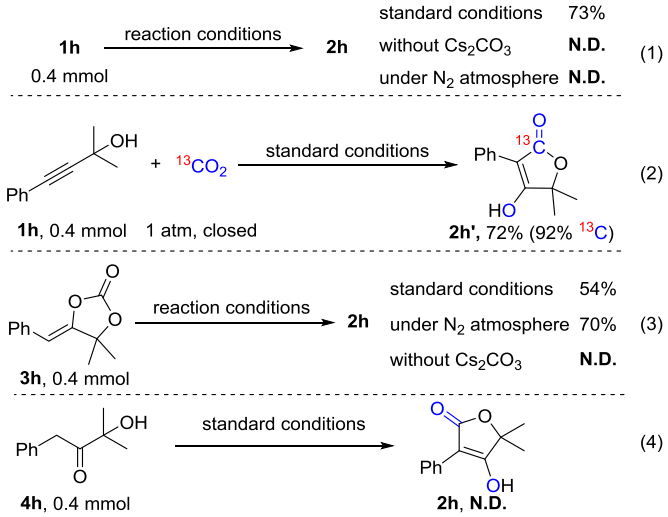
**Table 2** Substrate scope [a]




[a] Reaction conditions: propargylic alcohol **1** (0.4 mmol), $Cs_2CO_3$ (4 equiv.), 1 atm of $CO_2$, 3 mL of DMI, 48 h, 65 °C. Yield of isolated products. [b] $Cs_2CO_3$ (2 equiv.). [c] 2 h. [d] The yield of gram-scale reaction.

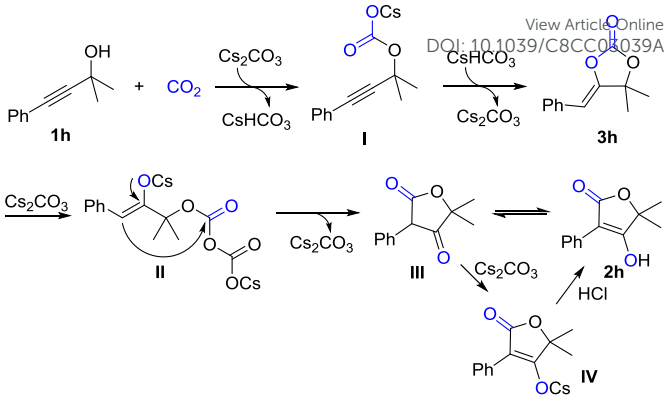
To gain more insight into the reaction mechanism, a series of control experiments were conducted (Scheme 2). Firstly, **2h** could not be formed either under $N_2$ atmosphere or in the absence of base, highlighting the crucial role of $CO_2$ and base in this transformation (eq. 1). Moreover, **2h'** was obtained with 92% $^{13}C$ label in 72% yield when $^{13}CO_2$ was used (please see ESI for more details), which clearly indicated that the carbonyl group came from $CO_2$ (eq. 2). Since we detected 5-benzylidene-4,4-dimethyl-1,3-dioxolan-2-one **3h**, which was

reported as the desired product in previous works,[3-13] in some cases with different reaction conditions, we further investigated the role of this species. We found that the tetronic acid product **2h** could be obtained in moderate to good yield in the reaction of **3h** under either standard conditions or $N_2$ atmosphere (eq. 3). These results indicated that cyclic carbonate **3h** might be a competent intermediate. Notably, **2h** was not detected without $Cs_2CO_3$, indicating that the base is vital for the generation of tetronic acid from alkylidene cyclic carbonate (eq. 3). Moreover, 3-hydroxy-3-methyl-1-phenylbutan-2-one **4h**, another product in previous work,[15] afforded no desired product **2h** under standard reaction conditions, excluding the possibility of **4h** as the intermediate (eq. 4).




**Scheme 2** Control experiments

Based on the above results and previous works, the following possible mechanism is proposed with phenyl propargylic alcohol **1h** as the example (Scheme 3). In the basic reaction conditions, **1h** undergoes deprotonation and then reacts with $CO_2$ to generate carbonate **I**, which undergoes intramolecular ring-closing reaction to form the alkylidene cyclic carbonate intermediate **3h**. Nucleophilic attack of the carbonyl group in **3h** by carbonate anion and following ring-opening process give the intermediate **II**.[21] Then the Dieckmann-type condensation releases carbonate anion and gives the re-cyclized product **III**, which is in equilibrium with the desired tetronic acid **2h**. Further deprotonation by excess of $Cs_2CO_3$ would lead to enolate **IV**, which can be quenched by acid to generate **2h**. Although 1 equivalent of $Cs_2CO_3$ seems enough for this transformation (i.e. Table 1, entry 18), excess of $Cs_2CO_3$ (i.e. 2-4 equivalents) showed higher efficiency, which might arise from the solubility issue of $Cs_2CO_3$ in organic solvent or the low rate for the ring-opening process of alkylidene cyclic carbonate, i.e. **3h**.




**Scheme 3** Proposed mechanism

In conclusion, we have reported the first method for the synthesis of important tetronic acids from aryl propargylic alcohols with $CO_2$. This transition-metal-free and practical process takes place with easily-available and nontoxic starting materials, high atom-economy and step-economy under mild reaction conditions. Besides, this novel method generates the important products with good functional group tolerance and high yields. Preliminary mechanistic studies suggest that the reaction proceeds via cyclization, ring-opening and re-cyclization processes. Further mechanistic studies are underway in our laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We thank the National Natural Science Foundation of China (21502124), the "973" Project from the MOST of China (2015CB856600), the "1000-Youth Talents Program", the Fundamental Research Funds for the Central Universities, the Sichuan Provincial Department of Education (17ZA0219) and Neijiang Normal University (KF10076) for financial support. We also thank the comprehensive training platform of the Specialized Laboratory in the College of Chemistry at Sichuan University for compound testing.

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20 CCDC 1815711 (**2h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

21 Yamada group has reported that cyclic carbonates could be hydrolyzed in the presence of aqueous NaOH to afford the ring-opening α-hydroxyl ketones, more information please see SI in ref. 3(*b*).