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Palladium-Catalyzed Oxidative C≡C Triple Bond Cleavage of 2-Alkynyl Carbonyl Compounds Toward 1,2-Dicarbonyl Compounds

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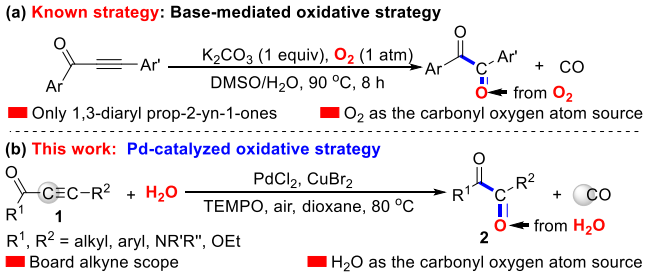
Dedicated to Professor Qing-Yun Chen on the occasion of his 90th birthday

A new, general palladium-catalyzed oxidative strategy for the cleavage of the C≡C triple bond is presented. By employing $PdCl_2$, $CuBr_2$, TEMPO and air as the catalytic system and H_2O as the carbonyl oxygen atom source, a wide range of 2-alkynyl carbonyl compounds, including 1,3-disubstituted prop-2-yn-1-ones, propiolamides and propiolates, lost an alkynyl carbon to access various 1,2-dicarbonyl compounds, e.g., 1,2-diones, 2-keto amides and 2-keto esters, through Wacker oxidation, intramolecular cyclization and C-C bond cleavage cascades.

Background and Originality Content

Alkynes are importantly common chemical feedstocks that have been widely used in synthetic community. Accordingly, the development of methods for transformations of alkynes to increase molecular complexity and construct functional molecules has attracted ongoing attention.[1-9] Attractive methods include transformations of alkynes by cleavage of the C≡C triple bonds.[2-8] Although the cleavage of the C≡C triple bond of alkynes has been widely explored, it remains a great challenge of completely cleaving the C≡C triple bond and then functionalizing. Traditionally, the C≡C triple bond is cleaved by ligating to metal complexes and oxidative cleavage using a stoichiometric amount of metal reagents.[2,3] However, only a few papers[3-7] on the metal-catalyzed alkyne cleavage reactions have been reported except for metathesis of alkynes.[8] For example, the initial Rh-catalyzed alkynes cleavage protocol used additional 2-aminopyridine or 2-aminophenol to *in situ* react with alkynes leading to the C≡C triple bond cleavage.[3,4] Subsequently, 1,n-ynols were employed for the alkyne cleavage purpose by either Ru-catalyzed OH-elimination generating alkene and CO[5] or Au-catalyzed OH-addition leading to butenolides and acids.[6] Jiang and Wang have established a Lewis acid promoted palladium-catalyzed oxidative cleavage of alkynes with molecular oxygen to furnish esters in the presence of additional alcohols.[7a] Thus, the development of new metal-catalyzed alkynes cleavage transformations are still fascinated due to its cascade or domino strategy. In 2014, Cui and coworkers[7b] found a new radical strategy for the cleavage of the C≡C triple bonds where a combination of a base (K_2CO_3) with O_2 as both the oxidant and the carbonyl oxygen atom source enabled oxidative conversion of diaryl eth-2-yn-1-ones to 1,2-diketones (Scheme 1a). However, this method is limited to 1,3-diaryl prop-2-yn-1-ones probably because the in-situ generation of the superoxide radical intermediates requires the aryl functional groups to activate them. Due to an interest in the palladium-catalyzed transformations of alkynes, and inspired by Wan's work which involved a new Wacker-type oxidation of alkynes mediated by $PdBr_2$ and $CuBr_2$,[9h-i] we accidentally found a C≡C triple bond cleavage using 2-alkynyl carbonyl compounds as the starting materials, which meanwhile led to an efficient approach to 1,2-dicarbonyl compounds through an alkynyl carbon-lost process (Scheme 1b).

Scheme 1 Oxidative transformations of 2-alkynyl carbonyl compounds.



Results and Discussion

Optimization of Reaction Conditions

We initiated our study by examining the reaction of 1,3-diphenylprop-2-yn-1-one (**1a**) with $PdCl_2$ and $CuBr_2$ in dioxane at 80 °C under air atmosphere: we were pleased to find that an unexpected benzil (**2a**) was isolated in 16% yield (entry 1 in Table 1). Distinctly, benzil (**2a**) is generated by a carbon-lost process from 1,3-diphenylprop-2-yn-1-one (**1a**), which may proceed *via* the oxidative cleavage of the C≡C triple bond. Based on these considerations, several oxidants, TEMPO, TBHP, DDQ and $K_2S_2O_8$, were investigated (Table S1; Supporting Information). Screening revealed that TEMPO displayed the highest activity: treatment of substrate **1a** with 10 mol% of $PdCl_2$, 1.2 equiv of $CuBr_2$ and 1.2 equiv of TEMPO afforded benzil (**2a**) in 82% yield (entry 2). Among the effects of Pd and Cu examination, it turned out that the reaction was carried out at 10 mol% of $PdCl_2$ and 1.2 equiv of $CuBr_2$, providing the best results (entries 2-9). Screening revealed that the amount of water in dioxane influenced the reaction in terms of yield: the yield of **2a** was lowered to 66% using 0.25 mL of H_2O and 61% in 2 mL of H_2O (entries 2, 10 and 11). Notably, the reactivity of substrate **1a** was decreased under either O_2 or argon atmosphere, suggesting that air can facilitate the reaction (entries 12 and 13). It is noteworthy that the Cu salt acts as a promoter as without it the reaction could occur in 31% yield (entry 14). However, Pd catalysts were crucial because omission of them the

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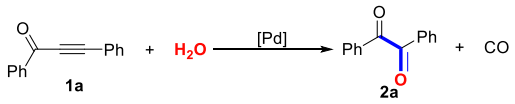
reaction could not take place (entry 15).

Table 1 Screening of the optimal reaction conditions[a]



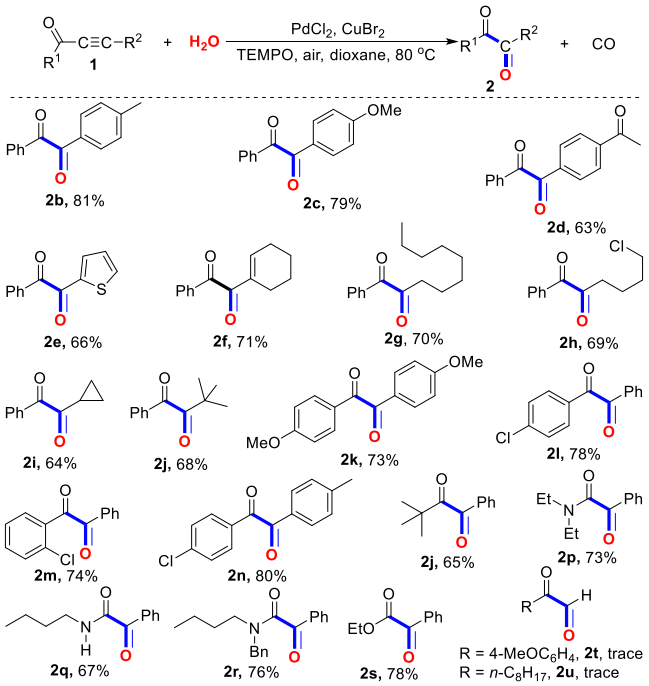
Entry	[Pd] (mol%)	[Cu]	Solvent (v/v)	Yield (%)[b]
1[c]	$PdCl_2$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	16
2	$PdCl_2$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	82
3	$PdCl_2$ (15)	$CuBr_2$	H_2O/dioxane (1/4)	81
4	$PdCl_2$ (5)	$CuBr_2$	H_2O/dioxane (1/4)	71
5	$PdBr_2$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	78
6	$Pd(OAc)_2$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	71
7	$Pd(PPh_3)_4$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	68
8	$PdCl_2$ (10)	$CuCl_2$	H_2O/dioxane (1/4)	58
9	$PdCl_2$ (10)	$Cu(OAc)_2$	H_2O/dioxane (1/4)	41
10	$PdCl_2$ (10)	$CuBr_2$	H_2O/dioxane (1/9)	66
11	$PdCl_2$ (10)	$CuBr_2$	H_2O/dioxane (4/1)	61
12[d]	$PdCl_2$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	68
13[e]	$PdCl_2$ (10)	$CuBr_2$	H_2O/dioxane (1/4)	56
14	$PdCl_2$ (10)	—	H_2O/dioxane (1/4)	31
15	—	$CuBr_2$	H_2O/dioxane (1/4)	0

[a] Reaction conditions: **1a** (0.3 mmol), [Pd], [Cu] (1.2 equiv), TEMPO (1.2 equiv), and H_2O/solvent (2.5 mL) at 80 °C for 36 h under air atmosphere. [b] Isolated yield. [c] Without TEMPO. [d] Under O_2 (1 atm) atmosphere. [e] Under argon atmosphere.

As shown in Table 2, the generality of this Pd-catalyzed oxidative C≡C triple bond cleavage protocol with regard to 2-alkynyl carbonyl compounds was investigated under the optimal reaction conditions. A variety of 3-oxoprop-1-ynyl compounds, including 2-yn-1-ones, propiolamides and propiolate, successfully underwent the reaction in moderate to good yields (Products **2b-s**). Using 10 mol % of $PdCl_2$, 1.2 equiv of $CuBr_2$ and 1.2 equiv of TEMPO, a number of substituents, such as electron-rich or electron-deficient aryl, heteroaryl, vinyl and aliphatic groups, at the terminal alkyne moiety of 2-yn-1-ones were all tolerated (**2b-2j**). We found that substituents, including Me, MeO and MeCO, on the aryl ring were well tolerated (**2b-d**), and the electron-withdrawing MeCO group showed lower reactivity than the electron-donating groups (e.g., Me, MeO). While alkyne bearing a *p*-methoxyphenyl group reacted with $PdCl_2$, $CuBr_2$, TEMPO and air smoothly to furnish the desired product **2c** in 79% yield, alkyne with an acetyl (MeCO) group diminished the yield of **2d** to 63%. Notably, the introduction of a heterocycle or a cyclohex-1-en-1-yl group into this system were also efficient for accessing **2e-f** in good yields, which makes this methodology more valuable for the preparation of pharmaceuticals and nature products. We were pleased to find that internal 2-alkyl-1-arylacetylenes, such as 1-phenylundec-2-yn-1-one, 7-chloro-1-phenylhept-2-yn-1-one, 3-cyclopropyl-1-phenylprop-2-yn-1-one and bulky 4,4-dimethyl-1-phenylpent-2-yn-1-one, were consistent with the optimal conditions, giving the corresponding products **2g-j** in high yields.

In light of the above results, substituents adjacent to the carbonyl moiety of 2-alkynyl carbonyl compounds were tested (**2k-s**). Using 1-arylprop-2-yn-1-one, possessing a *para*-MeO group, on the aryl ring was converted efficiently to **2k** in 73% yield. Gratifyingly, for 1-arylprop-2-yn-1-ones bearing a *para*- or an *ortho*-Cl group the reaction executed smoothly to afford **2l-n**, respectively, in 74-80% yields. Notably, the reaction of 1-(4-chlorophenyl)-3-(p-tolyl)prop-2-yn-1-one only furnished 1-(4-chlorophenyl)-2-(p-tolyl)ethane-1,2-dione **2n** in 80% yield, and the cross C≡C triple bond cleavage products, such as 1,2-dip-tolylethane-1,2-dione and 1,2-bis(4-chlorophenyl)ethane-1,2-dione, were not observed by GC-MS analysis. The results imply the reaction proceeds via an intramolecular C≡C triple bond cleavage process. The reaction was applicable to both propiolamides and propiolate, accessing the corresponding products **2o-2r** in good yields. Unfortunately, attempts to execute oxidative transformations of terminal ynones **1t-u** failed (**2t-2u**).

Table 2 Variation of the 2-alkynyl carbonyl compounds (**1**)[a]

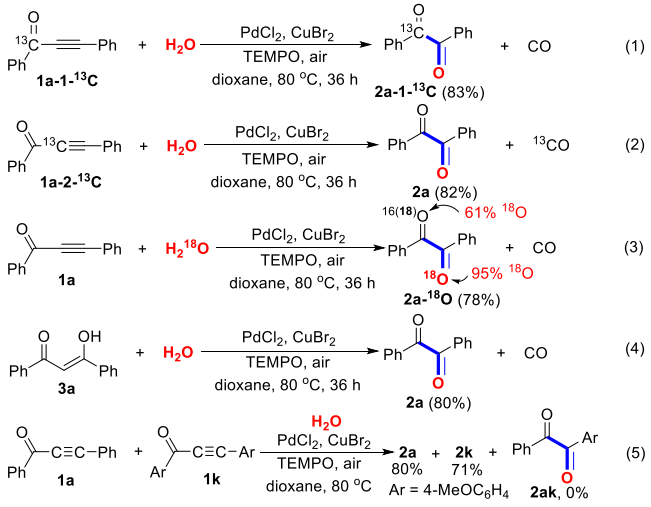


[a] Reaction conditions: **1a** (0.3 mmol), $PdCl_2$ (10 mol %), $CuBr_2$ (1.2 equiv), TEMPO (1.2 equiv), and H_2O/dioxane (1:4, 2.5 mL) at 80 °C for 36 h under air atmosphere.

To understand the mechanism, some controlled experiments were carried out (Scheme 2). Two ^{13}C-labeled experiments showed that the alkynyl carbon adjacent to the carbonyl group was lost during the C≡C triple bond cleavage process (eqs 1 and 2). Subsequently, treatment of substrate **1a** with $H_2{}^{18}O$, $PdCl_2$, $CuCl_2$, TEMPO and air afforded the corresponding ^{18}O-containing product **2a**-^{18}O determined by GC-MS analysis (eq 3). To our surprise, the HRMS analysis indicated that some of oxygen of the inherent carbonyl group of **1a** was replaced by ^{18}O (**2a**-^{18}O).[10] We found that a trace of 3-hydroxy-1,3-diphenylprop-2-en-1-one (**3a**) was observed by GC-MS analysis during the reaction of **1a** (Table 1). Thus, 3-hydroxy-1,3-diphenylprop-2-en-1-one (**3a**) was employed for the reaction in the presence of $PdCl_2$, $CuBr_2$, TEMPO and air: Indeed, substrate **3a** could be converted to the desired product **2a** in 80% yield (eq 4). This suggests that the reaction may proceed via the similar 3-hydroxy-prop-2-en-1-one intermediate.[11] Notably,

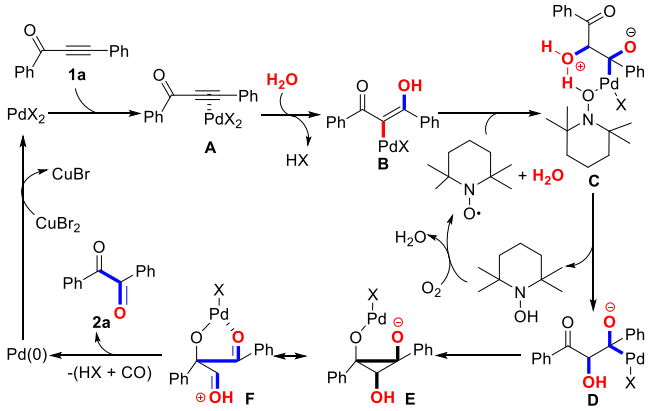
the cross reaction with ynones **1a** and **1k** gave no the cross product 2ak, supporting an intramolecular process (eq 5).

Scheme 2 Control Experiments



Therefore, a possible mechanism as outlined in Scheme 3 was proposed on the basis of the current results and the previously reported literatures. Complexation of $PdCl_2$ with alkyne **1a** generates intermediate **A**, followed by Wacker oxidation of the C≡C triple bond in the alkyne with H_2O to affords intermediate **B**.[11,12] Intermediate **B** undergoes the second Wacker reaction[13] with the aid of TEMPO to yield intermediate **C**, and then deprotonation to intermediate **D** and 2,2,6,6-tetramethylpiperidin-1-ol, in which TEMPO is regenerated from the oxidation of 2,2,6,6-tetramethylpiperidin-1-ol by O_2 (air). Intramolecular addition to the pre-existing carbonyl group of intermediate **D** results in intermediates **E** and **F**.[14] Finally, sequential decarbonylation and reductive elimination of intermediate **F** takes place leading to the desired product **2a**, CO, HX and Pd(0) species. Oxidation of the Pd(0) species by $CuBr_2$ regenerates the active Pd(II) species to start the new catalytic cycle.

Scheme 3 Possible mechanisms



Conclusions

In summary, we have described a novel palladium-catalyzed oxidative cleavage of the C≡C triple bond in 2-alkynyl carbonyl compounds for the synthesis of 1,2-dicarbonyl compounds using H_2O as the carbonyl oxygen atom source. This method employs an oxidative tandem strategy to allows a wide range of 2-alkynyl carbonyl compounds, including 1,3-disubstituted prop-2-yn-1-ones, propiolamides and propiolates, to undergo the C≡C triple bond cleavage with excellent selectivity and functional group compatibility. The mechanism was also discussed according to the ^{13}C-labeled and ^{18}O-labeled experiments.

Experimental

General experimental section.

2-Alkynyl carbonyl compounds **1** were prepared according to the known procedures.[15] All the other materials and solvents were purchased from commercial suppliers and used without additional purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (^1H at 500 MHz and ^{13}C at 125 MHz). NMR data were obtained in $CDCl_3$ unless otherwise noted. High-resolution mass spectra were recorded on a Bruker microTOF-QII (ESI) spectrometer. Preparative thin-layer chromatography was performed on silica gel plates with PF254 indicator. Flash column chromatography was performed with silica gel 60N unless otherwise noted.

Typical Experimental Procedure for Palladium-Catalyzed Oxidative Cleavage of the C≡C Triple Bond of 3-Oxoprop-1-ynyl Compounds (1):

To a Schlenk tube was added alkynes **1** (0.3 mmol), $PdCl_2$ (10 mol %), $CuBr_2$ (1.2 equiv), TEMPO (1.2 equiv) and dioxane (2.0 mL) and H_2O (0.5 mL) was stirred at 85 °C under air atmosphere for the indicated time (36 h) until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was filtered, washed with water, and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated in vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to afford the desired products **2**.

Analytical data for 2 and 3

(Main Text Paragraphs) Please include all the experimental details here excluding those in Supporting Information.

1,2-Diphenylethane-1,2-dione (2a):[16a] Green solid, mp: 94-95 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 4H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.5, 134.9, 132.9, 129.9, 129.0; IR (KBr, cm^{-1}): 1659; LRMS (EI 70 ev) *m*/*z* (%): 210 (M^+, 3), 105 (100), 77 (51), 51 (20).

1-Phenyl-2-*p*-tolylethane-1,2-dione (2b):[16a] Brown oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.7, 194.3, 146.2, 134.8, 133.0, 130.5, 129.9, 129.8, 129.7, 128.9, 21.9; IR (KBr, cm^{-1}): 1655, 1685; LRMS (EI 70 ev) *m*/*z* (%): 224 (M^+, 2), 119 (100), 105 (24), 91 (37).

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (2c):[16a] Green oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.97-7.93 (m, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.8, 193.1, 164.9, 134.6, 133.0, 132.3, 129.8, 128.8, 125.9, 114.3, 55.5; IR (KBr, cm^{-1}): 1668, 1593; LRMS (EI 70 ev) *m*/*z* (%): 240 (M^+, 1), 135 (100), 107 (11), 92 (13), 77 (38), 51 (9).

1-(4-Acetylphenyl)-2-phenylethane-1,2-dione (2d):[16b] Green oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.98 (s, 4H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.2, 193.7, 193.6, 141.2, 135.9, 135.1, 132.6, 130.0, 129.9, 129.1, 128.7, 26.9; IR (KBr, cm^{-1}): 1773, 1683; LRMS (EI 70 ev) *m*/*z* (%): 252 (M^+, 3), 147 (19), 119 (6), 105 (100), 91 (9), 77 (42), 43 (13).

1-Phenyl-2-(thiophen-3-yl)ethane-1,2-dione (2e):[16c] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 5.0 Hz, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.0, 185.6, 139.8, 136.9, 136.7, 134.8, 132.6, 130.2, 128.9, 128.8; IR (KBr, cm^{-1}):1685; LRMS (EI 70 ev) *m*/z (%): 216 (M^+, 7), 111 (49), 105 (100), 77 (45).

1-Cyclohexenyl-2-phenylethane-1,2-dione (2f): Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 6.77-6.76 (m, 1H), 2.33-2.30 (m, 2H), 2.22-2.18 (m, 2H), 1.67-1.58 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 196.5, 195.7, 149.9, 137.0, 134.5, 133.3, 129.6, 128.8, 26.6, 21.9, 21.4; IR (KBr, cm^{-1}): 2848, 1667, 1662; LRMS (EI 70 ev) *m*/z (%): 214 (M^+, 11), 105 (42), 109 (100), 81 (60), 77 (47), 51 (18); HRMS m/z (ESI) calcd for $C_{14}H_{15}O_2$ $[M+H]^+$ 215.1067, found 214.1073.

1-Phenyldecane-1,2-dione (2g):[16d] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 1.66-1.63 (m, 2H), 1.32-1.22 (m, 10H), 0.83 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.3, 192.3, 134.3, 131.8, 129.9, 128.6, 38.6, 31.5, 29.0, 28.9, 28.8, 22.6, 22.4, 13.8; IR (KBr, cm^{-1}): 2917, 2847, 1720, 1671; LRMS (EI 70 ev) *m*/z (%): 246 (M^+, 1), 141 (6), 105 (100), 77 (25), 71 (11), 57 (13).

6-Chloro-1-phenylhexane-1,2-dione (2h): Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 3.51 (t, *J* = 6.0 Hz, 2H), 2.87 (t, *J* = 7.0 Hz, 2H), 1.82-1.79 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.5, 192.0, 134.7, 131.8, 130.2, 128.9, 44.4, 37.7, 31.7, 20.2; IR (KBr, cm^{-1}): 2958, 1708, 1668; LRMS (EI 70 ev) *m*/z (%): 226 (M^++2, 1), 224 (M^+, 3), 105 (100), 77 (39), 51 (13); HRMS m/z (ESI) calcd for $C_{12}H_{14}{}^{35}ClO_2$ $[M+H]^+$ 225.0677, found 225.0815.

1-Cyclopropyl-2-phenylethane-1,2-dione (2i):[16e] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 2.49-2.46 (m, 1H), 1.27-1.24 (m, 2H), 1.14-1.11 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.6, 192.3, 134.5, 132.1, 130.2, 128.8, 18.6, 13.2; IR (KBr, cm^{-1}): 1691, 1675; LRMS (EI 70 ev) *m*/z (%): 174 (M^+, 2), 105 (100), 78 (4), 77 (48), 51 (19), 41 (21).

3,3-Dimethyl-1-phenylbutane-1,2-dione (2j):[16c] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75 (t, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 1.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.9, 195.4, 134.5, 132.8, 129.5, 128.9, 42.6, 26.2; IR (KBr, cm^{-1}): 2962, 1695, 1671; LRMS (EI 70 ev) *m*/z (%): 190 (M^+, 2), 105 (100), 85 (6), 77 (35), 57 (33), 51 (13).

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (2k):[16a] Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 4H), 6.96 (d, *J* = 9.0 Hz, 4H), 3.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 164.8, 132.3, 126.1, 114.2, 55.6; LRMS (EI, 70 eV) *m/z* (%): 270 (M^+, 3), 207 (4), 135 (100), 92(28).

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (2l):[16a] Brown solid, mp 82-83 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46-7.40 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.4, 192.5, 141.1, 134.6, 132.2, 130.8, 130.7, 129.4, 128.9, 128.6; IR (KBr, cm^{-1}): 1671, 1589; LRMS (EI 70 ev) *m*/z (%): 246 (M^++2, 1), 244 (M^+, 3), 139 (24), 111 (16), 105 (100), 77 (40), 75 (13), 51 (16).

1-(2-Chlorophenyl)-2-phenylethane-1,2-dione (2m):[16f] Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 3H), 7.33 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.1, 191.5, 134.1, 134.0, 133.4, 133.2, 131.8, 131.6, 130.0, 129.6, 128.4, 126.8; IR (KBr, cm^{-1}): 1673, 1592; LRMS (EI 70 ev) *m*/z (%): 246 (M^++2, 2), 244 (M^+, 7), 139 (25), 105 (100), 77 (44), 51 (17).

1-(4-Chlorophenyl)-2-*p*-tolylethane-1,2-dione (2n):[16g] Green solid, mp 101-102 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.6, 193.2, 146.4, 141.4, 131.4, 131.2, 130.3, 130.0, 129.8, 129.4, 21.9; IR (KBr, cm^{-1}): 1667; LRMS (EI 70 ev) *m*/z (%): 260 (M^++2, 1), 258 (M^+, 3), 119(100).

***N*,*N*-Diethyl-2-oxo-2-phenylacetamide (2p):**[16h] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 3.59-3.55 (m, 2H), 3.27-3.23 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.5, 166.7, 134.5, 133.2, 129.5, 128.9, 42.1, 38.8, 14.0, 12.8; IR (KBr, cm^{-1}): 1679, 1654; LRMS (EI 70 ev) *m*/z (%): 205 (M^+, 2), 105 (48), 100 (100), 77 (35) 72 (75).

***N*-Butyl-2-oxo-2-phenylacetamide (2q):**[16i] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.02 (brs, 1H), 3.35-3.31 (m, 2H), 1.54-1.50 (m, 2H), 1.36-1.32 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 187.9, 161.7, 134.3, 133.4, 131.2, 128.4, 39.1, 31.3, 20.0, 13.7; IR (KBr, cm^{-1}): 3388, 2954, 2921, 1664; LRMS (EI 70 ev) *m*/z (%): 205 (M^+, 12), 105 (100), 77 (38), 57 (25).

***N*-Benzyl-*N*-butyl-2-oxo-2-phenylacetamide (2r):** Green oil;^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (t, *J* = 4.5 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 4.5 Hz, 2H), 7.24-7.17 (m, 3H), 4.67 (s, 1H), 4.30 (s, 1H), 3.33 (t, *J* = 7.5 Hz, 1H), 3.00 (t, *J* = 7.5 Hz, 1H), 1.54-1.51 (m, 1H), 1.45-1.42 (m, 1H), 1.27 (t, *J* = 7.5 Hz, 1H), 1.07-1.02 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 1.5H), 0.67 (t, *J* = 7.5 Hz, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.4, 191.2, 167.3, 167.2, 136.2, 135.1, 134.5, 133.2, 130.0, 129.6, 129.5, 128.9, 128.9, 128.7, 128.6, 128.3, 128.2, 128.0, 127.8, 127.7, 51.0, 46.8, 46.6, 43.3, 29.9, 28.8, 20.0, 19.6, 13.7, 13.4; IR (KBr, cm^{-1}): 2962, 2929, 1683, 1634; LRMS (EI 70 ev) *m*/z (%): 295 (M^+, 2), 105 (37), 91 (100); HRMS m/z (ESI) calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1645, found 296.1657.

Ethyl 2-oxo-2-phenylacetate (2s):[16j] Green oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 4.40-4.35 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.4, 163.8, 134.8, 132.3, 129.9, 128.8, 62.3, 14.0; IR (KBr, cm^{-1}): 1736, 1683, 1200; LRMS (EI 70 ev) *m*/z (%): 178 (M^+, 1), 105 (100), 77 (48).

3-Hydroxy-1,3-diphenylprop-2-en-1-one (3a):[16k] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 16.92 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 4H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 4H), 6.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 185.6, 135.3, 132.3, 128.5, 127.0, 93.0; LRMS (EI 70 ev) *m*/z (%): 224 (M^+, 65), 223 (80), 147 (38), 105 (100).

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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[14] The controlled experiments (eq S2 of Scheme S1 in Supporting Information) show that $CuBr_2$ as a catalyst takes part in the reaction besides as an oxidant (another mechanism was proposed in Scheme S2). Moreover, TEMPO is necessary in the reaction of **3a**. A paper has reported on an example of $AlCl_3$ or $Cu(OAc)_2$-mediated decar-oxylation of 1,3-diphenylpropane-1,2,3-trione leading to benzil **2a**, see: Robertsd, J. D.; Smith, D. R.; Lee, C. C. The Decarbonylation of Diphenyl Triketone. *J. Am. Chem. Soc.* **1951**, *73*, 618–625. However, $PdCl_2$ combined with $Cu(OAc)_2$ and TEMPO displayed lower activity for the present reaction (41% yield of **2a**, entry 9 in Table 1), and the $PdCl_2/AlCl_3$/TEMPO system was less effective (10% yield of **2a**, entry 18 in Table S1).

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Entry for the Table of Contents

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Palladium-Catalyzed Oxidative C≡C Triple Bond Cleavage of 2-Alkynyl Carbonyl Compounds Toward 1,2-Dicarbonyl Compounds

Ming-Bo Zhou,[†] Mu-Jia Luo,[†] Ming Hu, and Jin-Heng Li*

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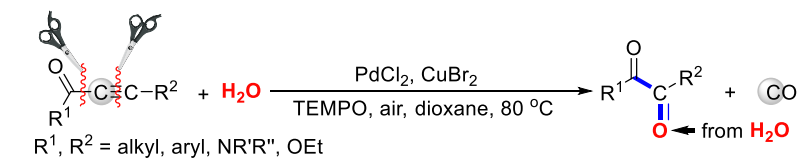

R^1, R^2 = alkyl, aryl, NR'R'', OEt

General: 19 exampes, up to 82% yield H_2O as the carbonyl oxygen atom source

New palladium-catalyzed oxidative strategy for the cleavage of the C≡C triple bond toward 1,2-dicarbonyl compounds, including 1,2-diones, 2-keto amides and 2-keto esters, is described, in which H_2O serves as the carbonyl oxygen atom source. This reaction is highlighted by its generality with respective to a wide range of 2-alkynyl carbonyl compounds, The mechanism was discussed according to the ^{13}C-labeled and ^{18}O-labeled experiments.

