

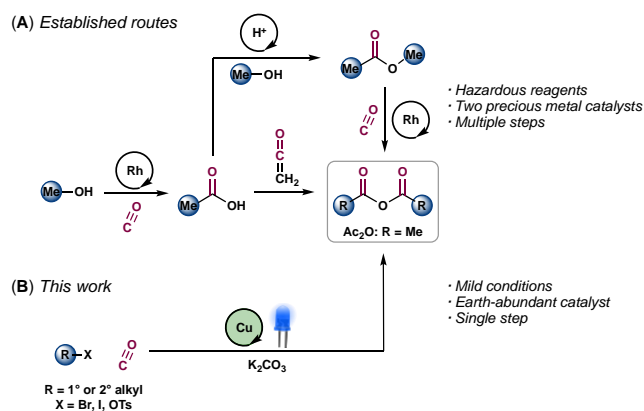
# Light-mediated synthesis of aliphatic anhydrides by Cu-catalyzed carbonylation of alkyl halides

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**ABSTRACT:** Acid anhydrides are valuable in the chemical industry for their role in synthesizing polymers, pharmaceuticals, and other commodities, but their syntheses often involve multiple steps with precious metal catalysts. The simplest anhydride, acetic anhydride, is currently produced by two Rh-catalyzed carbonylation reactions on bulk scale for its use in synthesizing products ranging from aspirin to cellulose acetate. Here, we report a light-mediated, Cu-catalyzed process for producing aliphatic, symmetric acid anhydrides directly by carbonylation of alkyl (pseudo-)halides in a single step without any precious metal additives. The transformation requires only simple Cu salts and abundant bases to generate a heterogeneous Cu<sup>0</sup> photocatalyst *in situ*, maintains high efficiency and selectivity upon scale up, and operates by a radical mechanism with several beneficial features. This discovery will enable engineering of bulk processes for producing commodity anhydrides efficiently and sustainably.

Acid anhydrides, the dehydrated forms of carboxylic acids, are ubiquitous in chemical synthesis. Their precisely tuned electrophilicity makes them reactive as acylating reagents yet stable enough for convenient handling. Acetic anhydride (Ac<sub>2</sub>O), the simplest acid anhydride, is produced on ~3 million tons/year scale due to its broad industrial applications<sup>1</sup>. It is widely used in pharmaceutical industries, especially for synthesizing analgesics such as aspirin<sup>2</sup> and paracetamol<sup>3</sup>. It is crucial for synthesizing cellulose acetate<sup>4</sup>, a biodegradable polymer extensively used in the food packaging and textile industries. Ac<sub>2</sub>O is also vital in the wood industry, where its hydrophobicity is exploited for use as a rot-resistant coating<sup>5</sup>. Thus, exploring convenient routes to synthesize commodity anhydrides has broad impact.



**Figure 1.** Acid anhydride syntheses: (A) Established industrial routes to acetic anhydride; (B) Photocatalytic synthesis of aliphatic anhydrides reported here.

One strategy for accessing anhydrides is to expose carboxylic acids to dehydrating reagents such as phosgene<sup>6</sup>, tosyl chloride<sup>7</sup>, isocyanate<sup>8</sup>, or thionyl chloride<sup>9</sup>. However, the high reactivity and toxicity of those reagents limit their broad applicability. Two main industrial routes to Ac<sub>2</sub>O have been implemented at

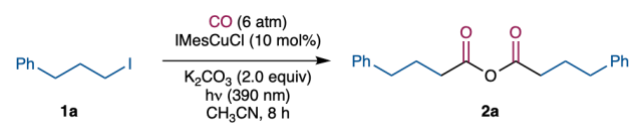
bulk scale (Figure 1A). One is based on the long-known reaction of acetic acid and ketene<sup>10</sup>, the latter of which is an unstable and toxic gas. The second is the Rh-catalyzed carbonylation of methyl acetate to synthesize Ac<sub>2</sub>O, a process developed by Tennessee Eastman in 1983 that remains the dominant source of Ac<sub>2</sub>O today<sup>11</sup>. The methyl acetate used in the Tennessee Eastman process typically derives from esterification of acetic acid, which is itself synthesized by the Monsanto process for Rh-catalyzed carbonylation of methanol<sup>12</sup>. The use of two Rh-catalyzed reactions and the need for isolation of two intermediates *en route* to Ac<sub>2</sub>O limit the sustainability and efficiency of this synthetic route.

Although most carbonylation reactions in industry utilize precious metal catalysts, recently there has been significant research effort toward developing carbonylation reactions catalyzed by non-precious metals that operate by different mechanisms and therefore enable complementary reactivity to emerge<sup>13</sup>. Our group has specialized in Cu-catalyzed carbonylation reactions, which allow carbonylative C-C and C-X coupling reactions of alkyl halides to occur *via* single electron transfer (SET) pathways involving alkyl and acyl radical intermediates<sup>14,15</sup>. Here, we report a Cu-catalyzed carbonylation method to convert alkyl (pseudo-)halides to aliphatic acid anhydrides in a single step using inexpensive copper halide salts as catalysts. The reaction takes place under photoexcitation by blue LED light in the presence of the abundant base, K<sub>2</sub>CO<sub>3</sub>, and under mild CO pressure. This discovery provides an efficient and sustainable route to commodity acid anhydrides that avoids precious metal catalysts or intermediate isolation steps (Figure 1B).

Previous Cu-catalyzed carbonylation reactions involve nucleophilic coupling partners that generate electron-rich organocopper(I) intermediates with sufficient reducing potential to engage alkyl halides in SET activation<sup>14</sup>. Here, we began our investigation by exposing 3-phenyl-1-iodopropane (**1a**) to Cu-catalyzed carbonylation conditions (CH<sub>3</sub>CN, 6 atm CO, 2 equiv. K<sub>2</sub>CO<sub>3</sub>, 10 mol% IMesCuCl) without any coupling

partner (Table 1). No reaction was observed at 70°C (entry 1), presumably due to a lack of any intermediate capable of doing SET with **1a**. We hypothesized that photoexcitation of the Cu catalyst would facilitate SET activation of **1a**.<sup>16,17</sup> Irradiating the reaction with blue LED light (390 nm) at room temperature resulted in 96% conversion to anhydride **2a** (entry 2). Although Cu-catalyzed carbonylation reactions have produced carboxylic acid derivatives such as esters<sup>18</sup>, amides<sup>19–23</sup>, and other acyl-X compounds<sup>24,25</sup>, there is no precedent for anhydride formation. Under Pd-catalyzed carbonylation conditions, aryl halides can be converted to anhydrides using carboxylate nucleophiles.<sup>26</sup> Similar results were observed with NaOH in place of K<sub>2</sub>CO<sub>3</sub> (entry 3), but little to no **2a** was observed when using alkoxide or amine bases (see Table S2). Next, we determined that the IMes ligand is not required, as quantitative conversion to **2a** was observed when using simple cuprous halide salts such as CuCl or CuBr·SMe<sub>2</sub> as catalysts without any added ligand (Table 1 entries 4–5, see also Table S1). On the other hand, no product was observed when Cu was omitted (Table 1 entry 6). For experimental convenience, we proceeded with CuBr·SMe<sub>2</sub> as the catalyst. Similar results were obtained with 4 h rather than 8 h reaction time, but 8 h was used for subsequent experiments to ensure complete conversion of all substrates. Importantly, a 15-fold scale-up of the reaction (entry 7) with substrate **1a** resulted in 87% conversion to **2a**, with the trace impurities being unreacted **1a** (6%), its corresponding alkyl bromide (5%), and the monocarbonylated ester product (2%).

**Table 1. Examination of selected reaction parameters<sup>a</sup>**



Entry	Variation(s)	Yield (%)
1	70°C, no hv	0
2	None	96
3	NaOH instead of K <sub>2</sub> CO <sub>3</sub>	83
4	CuCl instead of IMesCuCl	97
5	CuBr·SMe <sub>2</sub> instead of IMesCuCl	97
6	No catalyst	<5
7	CuBr·SMe <sub>2</sub> catalyst, 15x scaleup	87

<sup>a</sup>IMes = *N,N'*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene. Reactions were performed on 0.1-mmol scale unless otherwise noted; yields determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

With the optimized conditions, we examined the generality of the reaction towards different alkyl iodides (Figure 2A). Primary alkyl iodides with tethered aromatic rings provided moderate to excellent yields, with no significant impact from aromatic substituents (**1a–1d**). Aliphatic, primary alkyl iodides (**1e–1g**) were equally effective. Bulkier primary alkyl iodides (**1h–1i**) were successfully converted to the desired products, but with slightly lower yields. Both cyclic and acyclic secondary alkyl iodides (**1j–1m**) smoothly produced the corresponding products with moderate to good yields. Heterocyclic 4-iodotetrahydropyran (**1n**) was also tolerated under the reaction conditions. It should be noted that the yields for a few of the aforementioned substrates were reduced during the workup process due to product volatility. A beneficial feature of the

reaction is that the anhydride is typically produced in high purity, such that isolation involves simply filtering the crude product mixture and removing volatiles under reduced pressure. In experiments with methyl iodide as the substrate at 15x scale, we successfully detected 78% conversion to Ac<sub>2</sub>O (Figure 2A inset). Thus, we envision that an industrial-scale synthesis of Ac<sub>2</sub>O would be feasible under such mild and economical reaction conditions with appropriate reaction engineering.

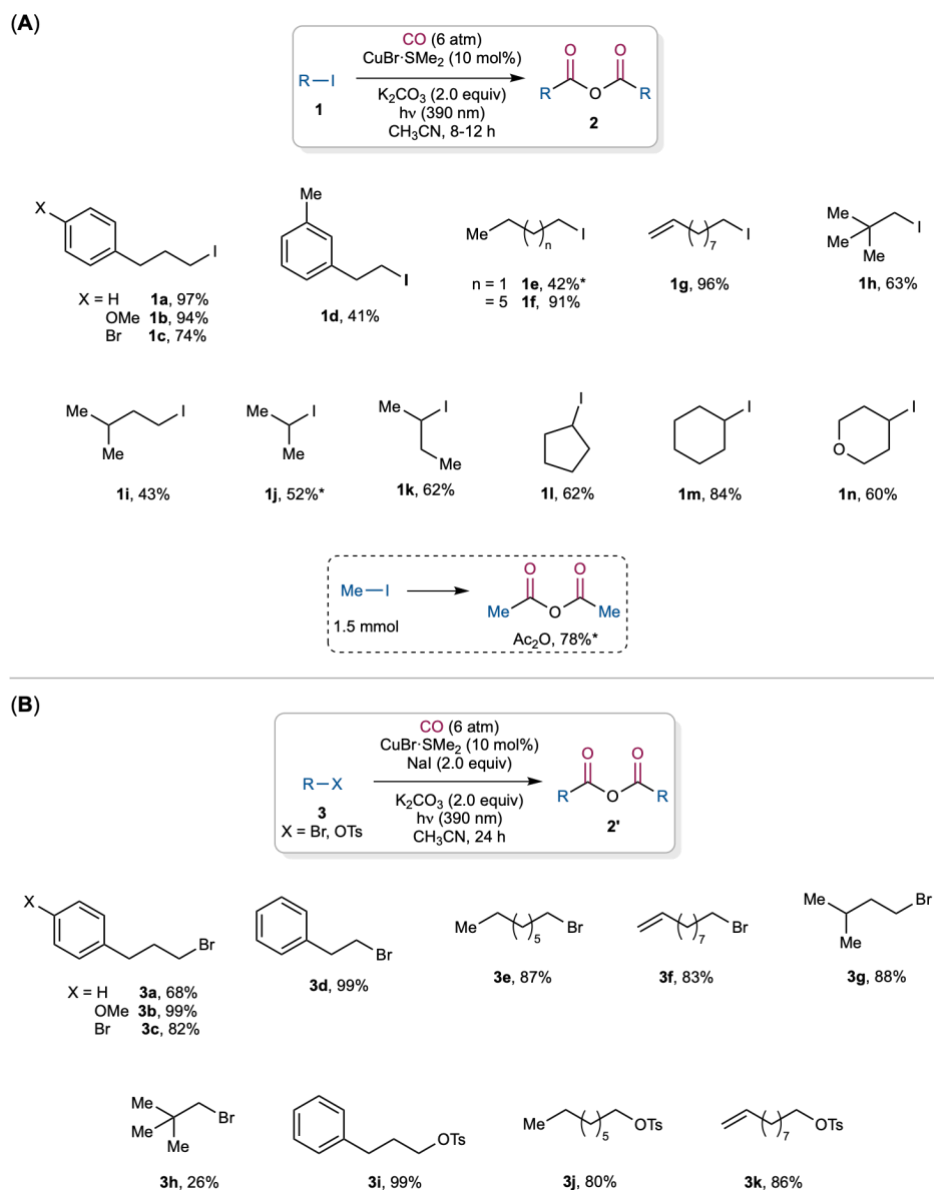
Next, we focused on alkyl electrophiles that are more abundant than iodides (Figure 2B). The alkyl bromide variant of **1a** was found to be inert toward the transformation. However, the desired products were obtained with high yields when NaI was used as an additive to generate alkyl iodide *in situ* (Finkelstein conditions)<sup>27</sup> with primary alkyl bromides (**3a–3g**), except for attenuated yield with bulky **3h**. Tertiary alkyl bromides and benzyl bromide were unsuccessful in delivering the corresponding anhydrides with or without NaI (see Supplementary Information). Taking inspiration from the Monsanto process, which uses alcohol as the alkyl source, we decided to test protected alcohols in our reaction. To our delight, various alkyl tosylates (**3i–3k**) were successfully converted into the related anhydrides in nearly quantitative yields with NaI additive. Both these conditions and the Monsanto and Tennessee Eastman processes require iodide additives to generate active electrophiles *in situ*, although the current method requires alkyl tosylate rather than free alcohols.

Having established the broad scope of the reaction, we turned our attention to the mechanism. Based on our initial experiments, we had already established that Cu<sup>I</sup> (pre-)catalyst and photoirradiation were required for the reaction to proceed (Table 1, entries 1 and 6). Furthermore, although K<sub>2</sub>CO<sub>3</sub> could donate either CO or CO<sub>2</sub> to the product in principle, this possibility was ruled out due to high yield obtained with NaOH in place of K<sub>2</sub>CO<sub>3</sub> (see Table 1, entry 3). Thus, we propose that the anhydride products incorporate two CO gas molecules plus an oxygen atom from the base. Noticing that solids typically precipitated from solution during the reaction, we next interrogated whether the transformation proceeds by homogeneous or heterogeneous catalysis using a filtration test<sup>28</sup> (Figure 3A, reaction i). Reactant **1a** was consumed quantitatively under optimized conditions at 4.5 h reaction time. Stopping the reaction at 1 h provided 51% consumption of **1a**. Filtering the reaction mixture at 1 h and then allowing it to further proceed to 4.5 h gave only 55% consumption of **1a**. Since reaction progress effectively halts upon filtration of the reaction mixture, we concluded that an *in-situ* generated heterogeneous catalyst material is responsible for mediating the observed transformation. A solid material was also found to form by exposing a 1:10 mixture of CuBr·SMe<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> (no alkyl iodide) to the photochemical reaction conditions. XPS analysis of the solid precipitate indicated the presence of Cu<sup>0</sup> (see Supporting Information), and so a working hypothesis is that Cu nanoparticles are the active catalysts under operating conditions<sup>29</sup>.

To verify that organic radical intermediates are involved in the reaction, we exposed cyclopropylmethyl iodide (**1o**) to the reaction conditions and obtained anhydride **2o** in which both alkyl groups were ring-opened (Figure 3A, reaction ii). To test whether the reaction proceeds *via* an ester intermediate akin to the Tennessee Eastman process, we tested the viability of 3-phenylpropyl 4-phenylbutanoate (**4**) and obtained no evidence for ester carbonylation to yield **2a** (reaction iii). On the other

hand, 4-phenylbutanoyl iodide (**5**) was found to be a viable intermediate, converting to **2a** with high efficiency under the optimized catalytic conditions. Further investigations indicated

that conversion of **5** to **2a** did not require CO gas, Cu catalyst, or photoirradiation (reaction iv).



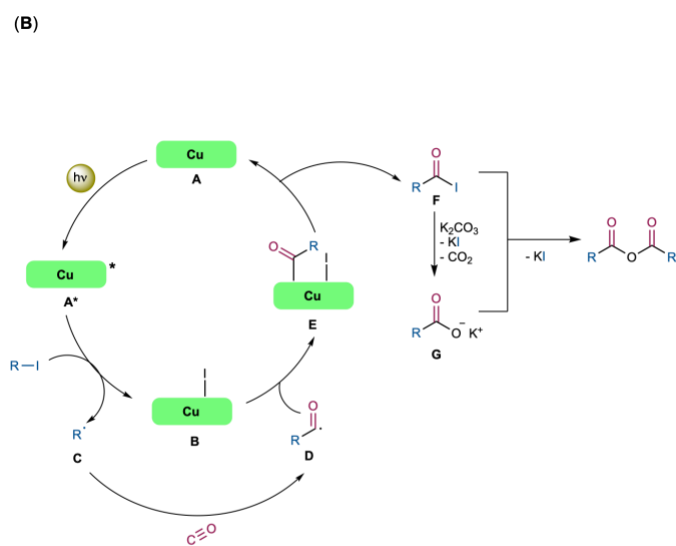
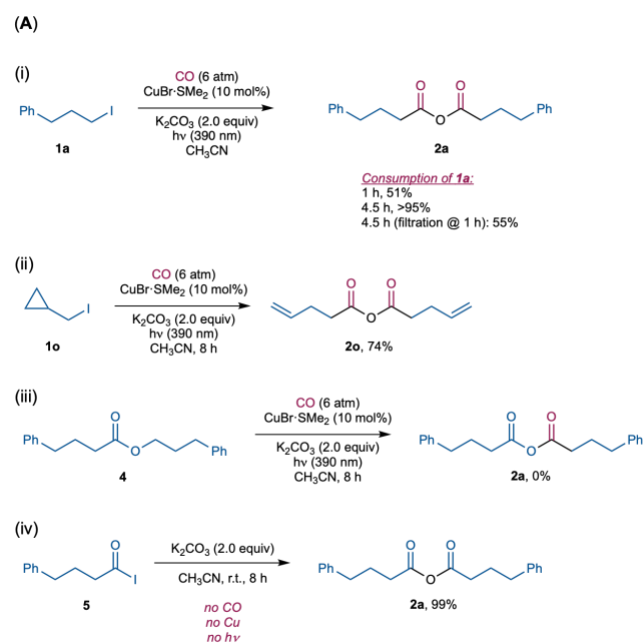
**Figure 2.** Substrate scope studies: (A) Scope in alkyl iodides; (B) Scope in alkyl bromides and tosylates in the presence of NaI additive.

Reactions were conducted on 0.1-mmol scale unless otherwise indicated. Yields were determined by <sup>1</sup>H NMR integration against an internal standard (CH<sub>2</sub>Br<sub>2</sub>) after silica gel filtration to remove inorganic catalysts and byproducts. \*Reaction time = 2 h. †Estimated yield due to volatility.

A common mechanism for obtaining the key acyl iodide intermediate from an alkyl iodide reactant is atom transfer carbonylation (ATC), a radical chain process<sup>30</sup>. However, our catalytic results are inconsistent with an ATC mechanism. Most importantly, ATC chemistry is efficient for secondary and especially tertiary alkyl halides but sluggish and unselective for primary alkyl and methyl halides, a pattern that has been attributed to the unfavorable thermodynamics of the halogen atom transfer step<sup>31</sup>. By contrast, the reaction reported here proceeds well for primary alkyl and methyl halides, less efficiently for secondary alkyl halides, and not at all for tertiary alkyl halides. Thus, we can rule out ATC and instead propose a Cu-centered mechanism<sup>14,15</sup> for alkyl iodide carbonylation (Figure 3B). The heterogeneous Cu catalyst **A** absorbs a photon

to produce excited-state **A\***, which is likely to be sufficiently reducing to engage the alkyl halide in SET<sup>16,17,29</sup>, producing iodine-adsorbed intermediate **B** and free alkyl radical **C**. Upon carbonylation, acyl radical **D** is formed. Rebound of **D** with **B** produces intermediate **E** with acyl and iodine group co-adsorbed on the catalyst surface. Subsequent C-I coupling regenerates **A** after desorption of acyl iodide **F**. Related mechanisms for light-mediated, Pd-catalyzed acyl halide formation have been proposed by Arndsten<sup>32,33</sup>, albeit with a homogeneous rather than heterogeneous catalyst. Next, as demonstrated in our metal-free dark reaction (Figure 3A, reaction iv), reaction of **F** with K<sub>2</sub>CO<sub>3</sub> with concomitant decarboxylation will form carboxylate **G**, which finally undergoes condensation with **F** to yield the anhydride product.

It is interesting to note that, in the absence of base, no acyl iodide formation is observed and only alkyl iodide is recovered (see Table S2). From this, we can conclude that acyl iodide



**Figure 3.** Mechanistic studies: (A) Experimental results probing the catalytic mechanism; (B) A plausible mechanism.

In addition to enabling carbonylation of primary alkyl and methyl halides in the absence of precious metals, a critical feature of the photocatalytic Cu conditions is the mild temperature at which the reaction proceeds. Carboxylate intermediate **G** is expected to react directly with the alkyl iodide partner to form an ester byproduct at slightly elevated temperatures<sup>34</sup>. Thus, the high anhydride selectivity is enabled by the light-mediated conditions that access reactivity at ambient temperature. We expect that replacement of  $K_2CO_3$  with other weak nucleophiles will provide access to other acyl pseudohalide products, and such explorations are currently underway.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures & spectral data (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

## ACKNOWLEDGMENT

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

formation is reversible under the photocatalytic conditions and driven forward by reaction with carboxylate **G**.

under Award Number DE-SC0021055. Dr. Igor Bolotin (UIC) assisted with XPS analysis.

## REFERENCES

- (1) *Acetic Anhydride Market Size, Share, Price Trends & Forecast 2021-2026*. <https://www.imarcgroup.com/acetic-anhydride-market-report> (accessed 2022-11-30).
- (2) Olmsted, J. A. I. Synthesis of Aspirin: A General Chemistry Experiment. *J. Chem. Educ.* **1998**, *75* (10), 1261. <https://doi.org/10.1021/ed075p1261>.
- (3) Friderichs, E.; Christoph, T.; Buschmann, H. Analgesics and Antipyretics. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2007. [https://doi.org/10.1002/14356007.a02\\_269.pub2](https://doi.org/10.1002/14356007.a02_269.pub2).
- (4) Fischer, S.; Thümmel, K.; Volkert, B.; Hettrich, K.; Schmidt, I.; Fischer, K. Properties and Applications of Cellulose Acetate. *Macromol. Symp.* **2008**, *262* (1), 89–96. <https://doi.org/10.1002/masy.200850210>.
- (5) Tullo, A. H. Making-Wood-Last-Forever-Acetylation. *Chemical & Engineering News*. <https://cen.acs.org/articles/90/i32/Making-Wood-Last-Forever-Acetylation.html> (accessed 2022-11-30).
- (6) Kocz, R.; Roestamadji, J.; Mobashery, S. A Convenient Triphosgene-Mediated Synthesis of Symmetric Carboxylic Acid Anhydrides. *J. Org. Chem.* **1994**, *59* (10), 2913–2914. <https://doi.org/10.1021/jo00089a046>.
- (7) Kazemi, F.; Sharghi, H.; Nasser, M. A. A Cheap, Simple and Efficient Method for the Preparation of Symmetrical Carboxylic Acid Anhydrides. *ChemInform* **2004**, *35* (23). <https://doi.org/10.1002/chin.200423101>.
- (8) Keshavamurthy, K. S.; Vankar, Y. D.; Dhar, D. N. Preparation of Acid Anhydrides, Amides, and Esters Using Chlorosulfonyl Isocyanate as a Dehydrating Agent. *Synthesis* **1982**, *1982* (6), 506–508. <https://doi.org/10.1055/s-1982-29859>.
- (9) Kazemi, F.; Kiasat, A. R.; Mombaini, B. Simple Preparation of Symmetrical Carboxylic Acid Anhydrides by Means of  $Na_2CO_3$

- /SOCl<sub>2</sub>. *Synth. Commun.* **2007**, *37* (18), 3219–3223. <https://doi.org/10.1080/00397910701547904>.
- (10) Hurd, C. D.; Dull, M. F. The Use Of Ketene In The Preparation Of Simple And Mixed Acid Anhydrides. *J. Am. Chem. Soc.* **1932**, *54* (8), 3427–3431. <https://doi.org/10.1021/ja01347a066>.
- (11) Zoeller, J. R.; Agreda, V. H.; Cook, S. L.; Lafferty, N. L.; Polichnowski, S. W.; Pond, D. M. Eastman Chemical Company Acetic Anhydride Process. *Catal. Today* **1992**, *13* (1), 73–91. [https://doi.org/10.1016/0920-5861\(92\)80188-S](https://doi.org/10.1016/0920-5861(92)80188-S).
- (12) Haynes, A. Acetic Acid Synthesis by Catalytic Carbonylation of Methanol. In *Catalytic Carbonylation Reactions*; Beller, M., Ed.; Topics in Organometallic Chemistry; Springer: Berlin, Heidelberg, 2006; pp 179–205. [https://doi.org/10.1007/3418\\_021](https://doi.org/10.1007/3418_021).
- (13) Li, Y.; Hu, Y.; Wu, X. F. Non-Noble Metal-Catalysed Carbonylative Transformations. *Chem. Soc. Rev.* **2018**, *47* (1), 172–194. <https://doi.org/10.1039/c7cs00529f>.
- (14) Cheng, L. J.; Mankad, N. P. Copper-Catalyzed Carbonylative Coupling of Alkyl Halides. *Acc. Chem. Res.* **2021**, *54* (9), 2261–2274. <https://doi.org/10.1021/acs.accounts.1c00115>.
- (15) Tung, P.; Mankad, N. P. Cu-Catalyzed C–C Bond Formation with CO; Topics in Organometallic Chemistry; Springer: Berlin, Heidelberg **2023**; pp 1–21. [https://doi.org/10.1007/3418\\_2023\\_84](https://doi.org/10.1007/3418_2023_84).
- (16) Hossain, A.; Bhattacharyya, A.; Reiser, O. Copper's Rapid Ascent in Visible-Light Photoredox Catalysis. *Science* **2019**, *364* (6439), eaav9713. <https://doi.org/10.1126/science.aav9713>.
- (17) Engl, S.; Reiser, O. Copper-Photocatalyzed ATRA Reactions: Concepts, Applications, and Opportunities. *Chem. Soc. Rev.* **2022**, *51* (13), 5287–5299. <https://doi.org/10.1039/D2CS00303A>.
- (18) Geng, H.-Q.; Wu, X.-F. Copper-Catalyzed Alkoxy carbonylation of Alkyl Iodides for the Synthesis of Aliphatic Esters: Hydrogen Makes the Difference. *Org. Lett.* **2021**, *23* (20), 8062–8066. <https://doi.org/10.1021/acs.orglett.1c03071>.
- (19) Zhao, S.; Mankad, N. P. Synergistic Copper-Catalyzed Reductive Aminocarbonylation of Alkyl Iodides with Nitroarenes. *Org. Lett.* **2019**, *21* (24), 10106–10110. <https://doi.org/10.1021/acs.orglett.9b04092>.
- (20) Yuan, Y.; Zhao, F.; Wu, X.-F. Copper-Catalyzed Enantioselective Carbonylation toward  $\alpha$ -Chiral Secondary Amides. *Chem. Sci.* **2021**, *12* (38), 12676–12681. <https://doi.org/10.1039/D1SC04210F>.
- (21) Geng, H.-Q.; Wu, X.-F. Copper-Catalyzed Hydroaminocarbonylation of Benzyldenecyclopropanes: Synthesis of  $\gamma,\delta$ -Unsaturated Amides. *Chem. Commun.* **2022**, *58* (45), 6534–6537. <https://doi.org/10.1039/D2CC02301F>.
- (22) Wu, F.-P.; Wu, X.-F. Ligand-Controlled Copper-Catalyzed Regiodivergent Carbonylative Synthesis of  $\alpha$ -Amino Ketones and  $\alpha$ -Boryl Amides from Imines and Alkyl Iodides. *Angew. Chem. Int. Ed.* **2021**, *60* (2), 695–700. <https://doi.org/10.1002/anie.202012251>.
- (23) Yuan, Y.; Wu, F.-P.; Schünemann, C.; Holz, J.; Kamer, P. C. J.; Wu, X.-F. Copper-Catalyzed Carbonylative Hydroamidation of Styrenes to Branched Amides. *Angew. Chem. Int. Ed.* **2020**, *59* (50), 22441–22445. <https://doi.org/10.1002/anie.202010509>.
- (24) Cheng, L. J.; Zhao, S.; Mankad, N. P. One-Step Synthesis of Acylboron Compounds via Copper-Catalyzed Carbonylative Borylation of Alkyl Halides. *Angew. Chem. - Int. Ed.* **2021**, *60* (4), 2094–2098. <https://doi.org/10.1002/anie.202012373>.
- (25) Cheng, L.-J. J.; Mankad, N. P. Cu-Catalyzed Carbonylative Silylation of Alkyl Halides: Efficient Access to Acylsilanes. *J. Am. Chem. Soc.* **2020**, *142* (1), 80–84. <https://doi.org/10.1021/jacs.9b12043>.
- (26) Brennfürer, A.; Neumann, H.; Beller, M. Palladium-Catalyzed Carbonylation Reactions of Aryl Halides and Related Compounds. *Angew. Chem. Int. Ed.* **2009**, *48* (23), 4114–4133. <https://doi.org/10.1002/anie.200900013>.
- (27) Finkelstein, H. Darstellung Organischer Jodide Aus Den Entsprechenden Bromiden Und Chloriden. *Berichte Dtsch. Chem. Ges.* **1910**, *43* (2), 1528–1532. <https://doi.org/10.1002/cber.19100430257>.
- (28) Widegren, J. A.; Finke, R. G. A Review of the Problem of Distinguishing True Homogeneous Catalysis from Soluble or Other Metal-Particle Heterogeneous Catalysis under Reducing Conditions. *J. Mol. Catal. Chem.* **2003**, *198* (1–2), 317–341. [https://doi.org/10.1016/S1381-1169\(02\)00728-8](https://doi.org/10.1016/S1381-1169(02)00728-8).
- (29) Gawande, M. B.; Goswami, A.; Felpin, F.-X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chem. Rev.* **2016**, *116* (6), 3722–3811. <https://doi.org/10/gg3fqf>.
- (30) Ryu, I. Radical Carboxylations of Iodoalkanes and Saturated Alcohols Using Carbon Monoxide. *Chem. Soc. Rev.* **2001**, *30* (1), 16–25. <https://doi.org/10.1039/a904591k>.
- (31) Matsubara, H.; Ryu, I.; Schiesser, C. H. An Ab Initio and DFT Study of Some Halogen Atom Transfer Reactions from Alkyl Groups to Acyl Radical. *Org. Biomol. Chem.* **2007**, *5* (20), 3320–3324. <https://doi.org/10.1039/b710449a>.
- (32) Liu, Y.; Zhou, C.; Jiang, M.; Arndtsen, B. A. Versatile Palladium-Catalyzed Approach to Acyl Fluorides and Carbonylations by Combining Visible Light- and Ligand-Driven Operations. *J. Am. Chem. Soc.* **2022**, *144* (21), 9413–9420. <https://doi.org/10.1021/jacs.2c01951>.
- (33) Torres, G. M.; Liu, Y.; Arndtsen, B. A. A Dual Light-Driven Palladium Catalyst: Breaking the Barriers in Carbonylation Reactions. *Science* **2020**, *368* (6488), 318–323. <https://doi.org/10.1126/science.aba5901>.
- (34) Hennis, H. E.; Easterly, J. P. Jr.; Collins, L. R.; Thompson, L. R. Esters from Reactions of Alkyl Halides and Salts of Carboxylic Acids. Reactions of Primary Alkyl Chlorides and Sodium Salts of Carboxylic Acids. *IEC Prod. Res. Dev.* **1967**, *6* (3), 193–195. <https://doi.org/10.1021/i360023a012>.

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