OL | Organic Letters

pubs.acs.org/OrgLett

Letter

Formal Enone α-Arylation via I(III)-Mediated Aryl Migration/Elimination

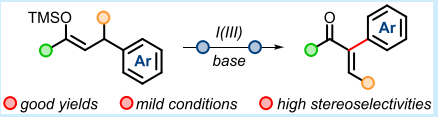
Bruna S. Martins,[†] Daniel Kaiser,[†] Adriano Bauer, Irmgard Tiefenbrunner, and Nuno Maulide*

Cite This: *Org. Lett.* 2021, 23, 2094–2098

Read Online

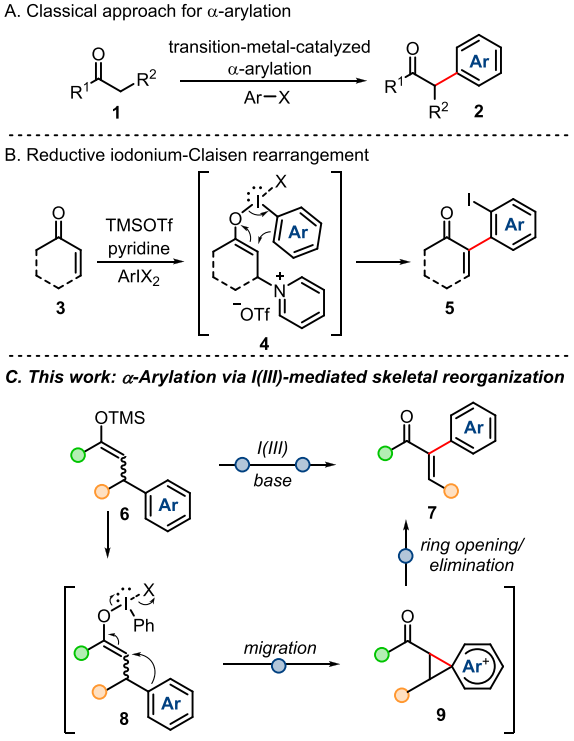
ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: A formal enone α-arylation is described. This metal-free transformation relies on the I(III)-mediated skeletal reorganization of silyl enol ethers and features mild conditions, good yields, and high stereoselectivities for β-substituted enones.



The development of novel approaches for the synthesis of α-arylated carbonyl compounds remains a topic of interest in synthetic chemistry. Whereas classical approaches rely on transition-metal-catalyzed couplings of carbonyl-derived enolates with aryl halides or pseudohalides (Scheme 1A),[1] complementary transition-metal-free methods based on electrophilic aromatic derivatives such as sulfur(IV),[2] bismuth(V),[3] iodine(III),[4] and arynes[5] have emerged in the last years. Alternative methodologies employing *N*-alkoxyenamines,[6] enolonium equivalents,[7] oxy-allyl cations,[8] and radical-mediated arylations[9] have also been developed.

Scheme 1. (A) Transition-Metal-Catalyzed Approach for α-Arylation of Carbonyl Compounds, (B) Enone Arylation *via* β-Pyridinium Enolonium Species, and (C) This Work: Enone α-Arylation *via* Iodine(III)-Mediated Aryl Migration/Elimination.



Despite the great progress achieved with transition-metal-free approaches, limitations in achievable substitution patterns and low atom economy still remain as drawbacks. In a recently disclosed elegant contribution by Wengryniuk and coworkers on the transition-metal-free α-arylation of enones, the direct C−H α-arylation occurs via the reductive iodonium Claisen rearrangement of *in-situ*-generated β-pyridinium silyl enol ethers (**4**) and $ArI(O_2CCF_3)_2$ reagents (Scheme 1B).[10] Although this method features high atom economy, comparably expedient substrate synthesis, and a broad arene scope, its modularity is limited by the inevitable presence of an *ortho*-iodo substituent and accompanying restrictions in the substitution pattern of the aromatic in addition to the need to prepare the iodoarenes.

As part of our long-standing interest in the rearrangements of high-energy intermediates, we have established methodologies for the iodine(III)-mediated α-arylation[11] and α-cyclopropanation[12] of carbonyl compounds through oxidative C−C bond activation and carbocationic rearrangements, respectively. Inspired by the outstanding ability of iodine(III)[13] in promoting oxidative rearrangements,[14] we wondered whether this class of reagents could evoke an intramolecular α-arylation of enones. Herein we report a practical transition-metal-free protocol for the formal α-arylation of enones via iodine(III)-mediated aryl migration/elimination.

Encouraged by our previous work on I(III)-mediated rearrangements,[11,12] we envisioned a process in which intermediate **9** (Scheme 1C), the product of aryl migration

Received: January 21, 2021
Published: February 26, 2021

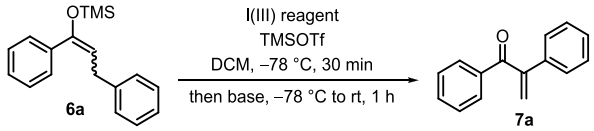
https://dx.doi.org/10.1021/acs.orglett.1c00251
Org. Lett. 2021, 23, 2094–2098

on enolonium species **8**, would undergo elimination to form **7**. We therefore started our investigations with the silyl enol ether **6a** as a model substrate and TMSOTf (trimethylsilyl trifluoromethanesulfonate) as the activator for a range of I(III) reagents (Table 1). The commercially available I(III) reagent PIDA (diacetoxyiodo)benzene, $PhI(OAc)_2$) gave a promising 50% yield of the desired α-arylated enone (entry 1). Increasing the amount of Et_3N (required for elimination) from 2 to 4 equiv led to the formation of **7a** in 74% yield (entry 2), and a screening of I(III) reagents revealed PIDA as the optimum oxidant for this transformation (entries 3−5).

Switching from Et_3N to either DIPEA (*N*,*N*-diisopropylethylamine) or NaOH did not lead to any improvement (entries 6 and 7); rather, through the presence of 35% β-triflated, α-arylated ketone, we were able to determine that the observed process likely proceeds *via* the capture of **9** by a triflate anion rather than direct elimination. It is additionally worth mentioning that during the examination of the conditions employing PIDA as the I(III) reagent, we observed the formation of distinct side products (α- and β-acetates), generated by competitive reactions with intermediates **8** and **9**.[11,12,15] Attempting to avoid the formation of these byproducts, we increased the amount of the activator TMSOTf, which led to an improved isolated yield (82%) of the α-arylated enone **7a** (entry 8).

With the optimized conditions in hand, we investigated the impact of electronics and sterics on the employed silyl enol ethers (Scheme 2). We first evaluated different substituents on the benzoyl moiety (Scheme 2a). Electron-donating, -withdrawing, and -neutral groups were all well tolerated, and the products **7a−j** were obtained in good yields regardless of the position of the substituent. Furthermore, a silyl enol ether

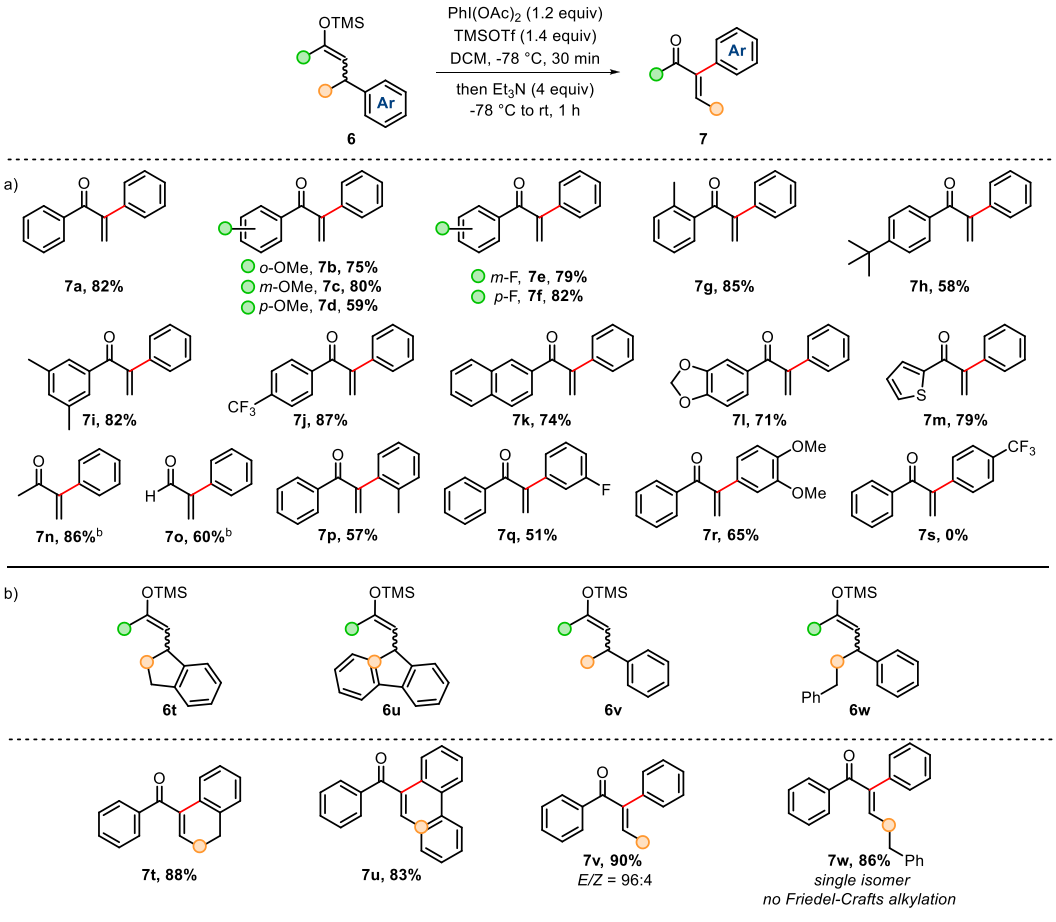
Table 1. Optimization of the Reaction Conditions[a]



entry	I(III) reagent[b]	TMSOTf (equiv)	base	yield (%)[g]
1	$PhI(OAc)_2$	1.2	Et_3N[c]	50
2	$PhI(OAc)_2$	1.2	Et_3N[d]	74
3	PhIO	1.2	Et_3N[d]	70
4	$PhI(OPiv)_2$	1.2	Et_3N[d]	56
5	$PhI(OCOCF_3)_2$	1.2	Et_3N[d]	24
6	$PhI(OAc)_2$	1.2	DIPEA[d,e]	38
7	$PhI(OAc)_2$	1.2	NaOH[f]	12
8	$PhI(OAc)_2$	1.4	Et_3N[d]	82[h]

[a]All screening was performed on 0.2 mmol of **6a** (1 equiv) in 2 mL of DCM (0.1 M). [b]1.2 equiv. [c]2 equiv. [d]4 equiv. [e]Alongside 35% β-trifate. [f]1 M, 4 equiv. [g]NMR yields. [h]Isolated yield. TMSOTf = trimethylsilyl trifluoromethanesulfonate. DIPEA = *N*,*N*-diisopropylethylamine. DCM = dichloromethane.

Scheme 2. Scope of I(III)-Mediated α-Arylation of Enones[a]



[a]All yields refer to pure, isolated products, unless otherwise stated. [b]NMR yields were determined using mesitylene as an internal standard.

https://dx.doi.org/10.1021/acs.orglett.1c00251
Org. Lett. 2021, 23, 2094−2098

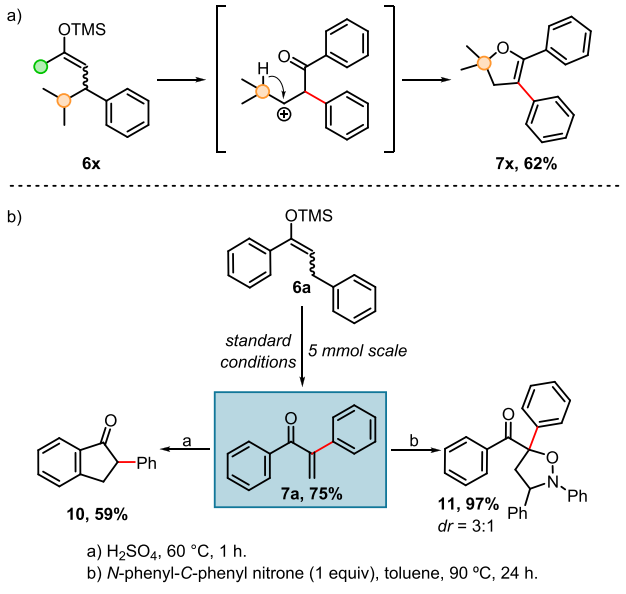
bearing a disubstituted aromatic ring was also susceptible to rearrangement in high yield (**7i**). Substrates bearing more elaborate aromatic rings such as 2-naphthyl (**7k**) and 1,3-benzodioxol-5-yl (**7l**) were also successfully transformed, as was 2-thienoyl-derived substrate (**7m**). In addition, an alkyl α-arylated enone **7n** and an enal **7o** were formed in 86 and 60% yield, respectively.[16]

Next, we evaluated the migration of substituted aryl groups. The rearrangement of an *o*-tolyl moiety afforded the product **7p** in 57% yield, whereas the migration of a *m*-fluoro derivative provided the enone **7q** in 51% yield. Additionally, the migration of a disubstituted aromatic group was accomplished effectively, yielding enone **7r** in 65%. Unfortunately, the shift of an electron-poor aryl group such as *p*-$CF_3C_6H_4$ proved fruitless as a consequence of its diminished migratory ability. Instead, we obtained the corresponding β-arylated, α,β-unsaturated ketone as a major product under standard conditions.

Interestingly, we found that substrates with fused rings underwent I(III)-mediated aryl migration/ring expansion/elimination, leading to α-arylated enones **7t** and **7u** in high yields (Scheme 2b). Gratifyingly, the formal α-arylation of β-substituted enones proceeded readily, giving the desired products **7v** and **7w** in excellent yields and with excellent stereoselectivities. (See the Supporting Information for a rationalization of this selectivity.) It is worth highlighting that the product **7w** proved more reactive to aryl migration/elimination than to a competitive intramolecular Friedel–Crafts reaction. In the case of an *iso*-propyl-substituted silyl enol ether (**6x**), we found that 2,3-dihydrofuran **7x** was formed in 62% yield (Scheme 3a). We presume that this heterocycle was generated through a phenyl migration/Wagner–Meerwein rearrangement/cyclization sequence.

To explore the synthetic utility of the new method, we chose product **7a** for further derivatization (Scheme 3b). Scale up (5 mmol) of its preparation could be achieved without a significant decrease in yield. The enone **7a** subsequently readily underwent Nazarov cyclization or a (3 + 2)-cycloaddition reaction. The synthesis of 2-phenyl-1-indanone (**10**) was accomplished in 59% yield, whereas the cycloaddition of **7a** with *N*-phenyl-*C*-phenyl nitrone furnished the desired isoxazolidine **11** in an excellent yield of 97%.

Scheme 3. Occurrence of a Cyclization Product and Functionalizations of α-Arylated Enone 7a



In summary, we have developed a skeletal rearrangement-based methodology for the α-arylation of enones. The use of I(III) to mediate the aryl migration/elimination enabled the formation of a series of α-arylated enones in good yields under mild conditions. Furthermore, we demonstrated that our method is suitable for substrates bearing fused rings, promoting aryl migration/ring expansion/elimination, as well as for β-substituted silyl enol ethers, giving high yields and excellent stereoselectivities.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00251.

Experimental procedures, ^{1}H and ^{13}C NMR spectra, and characterization data of compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Nuno Maulide − *University of Vienna, Institute of Organic Chemistry, 1090 Vienna, Austria;* orcid.org/0000-0003-3643-0718; Email: nuno.maulide@univie.ac.at

Authors

Bruna S. Martins − *University of Vienna, Institute of Organic Chemistry, 1090 Vienna, Austria;* orcid.org/0000-0001-9143-4434

Daniel Kaiser − *University of Vienna, Institute of Organic Chemistry, 1090 Vienna, Austria;* orcid.org/0000-0001-8895-9969

Adriano Bauer − *University of Vienna, Institute of Organic Chemistry, 1090 Vienna, Austria;* orcid.org/0000-0002-3376-343X

Irmgard Tiefenbrunner − *University of Vienna, Institute of Organic Chemistry, 1090 Vienna, Austria*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c00251

Author Contributions

†B.S.M. and D.K. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Generous support of this research by the European Research Council (Horizon 2020, VINCAT CoG 682002 to N.M.), the Austrian Science Fund (P32607 to N.M.; Fellowship J 4202-N28 to D.K.), and Boehringer Ingelheim is acknowledged. We are grateful to the University of Vienna for its continued and generous support of our research programs.

■ REFERENCES

(1) (a) Bellina, F.; Rossi, R. Transition Metal-catalyzed Direct Arylation of Substrates with Activated sp^3-Hybridized C–H Bonds and Some of Their Synthetic Equivalents with Aryl Halides and Pseudohalides. *Chem. Rev.* **2010**, *110*, 1082–1146. (b) Johansson, C. C. C.; Colacot, T. J. Metal-Catalyzed α-Arylation of Carbonyl and

Related Molecules: Novel Trends in C−C Bond Formation by C−H Bond Functionalization. *Angew. Chem., Int. Ed.* **2010**, *49*, 676−707.
(2) (a) Huang, X.; Maulide, N. Sulfoxide-mediated α-Arylation of Carbonyl Compounds. *J. Am. Chem. Soc.* **2011**, *133*, 8510−8513. (b) Huang, X.; Patil, M.; Farès, C.; Thiel, W.; Maulide, N. Sulfur(IV)-Mediated Transformations: From Ylide Transfer to Metal-free Arylation of Carbonyl Compounds. *J. Am. Chem. Soc.* **2013**, *135*, 7312−7323. (c) Zawodny, W.; Teskey, C. J.; Mishevska, M.; Völkl, M.; Maryasin, B.; González, L.; Maulide, N. α-Functionalisation of Ketones Through Metal-free Electrophilic Activation. *Angew. Chem., Int. Ed.* **2020**, *59*, 20935−20939.
(3) Koech, P. K.; Krische, M. J. Phosphine Catalyzed α-Arylation of Enones and Enals Using Hypervalent Bismuth Reagents: Regiospecific Enolate Arylation via Nucleophilic Catalysis. *J. Am. Chem. Soc.* **2004**, *126*, 5350−5351.
(4) For a review on α-functionalization of carbonyl compounds using hypervalent iodine see: (a) Olofsson, B.; Merritt, E. A. α-Functionalization of Carbonyl Compounds Using Hypervalent Iodine Reagents. *Synthesis* **2011**, *2011* (4), 517−538. Selected applications using iodine(III) for α-arylation of carbonyl compounds: (b) Chen, K.; Koser, G. F. Direct and Regiocontrolled Synthesis of α-Phenyl Ketones from Silyl Enol Ethers and Diphenyliodonium Fluoride. *J. Org. Chem.* **1991**, *56*, 5764−5767. (c) Aggarwal, V. K.; Olofsson, B. Enantioselective α-Arylation of Cyclohexanones with Diaryl Iodonium salts: Application to the Synthesis of (−)-Epibatidine. *Angew. Chem., Int. Ed.* **2005**, *44*, 5516−5519. (d) Norrby, P.-O.; Petersen, T. B.; Bielawski, M.; Olofsson, B. α-Arylation by Rearrangement: On the Reaction of Enolates with Diaryliodonium Salts. *Chem. - Eur. J.* **2010**, *16*, 8251−8254. (e) Jia, Z.; Gálvez, E.; Sebastián, R. M.; Pleixats, R.; Álvarez-Larena, Á.; Martin, E.; Vallribera, A.; Shafir, A. An Alternative to the Classical α-Arylation: The Transfer of an Intact 2-Iodoaryl from $ArI(O_2CCF_3)_2$. *Angew. Chem., Int. Ed.* **2014**, *53*, 11298−11301. (f) Wu, Y.; Arenas, I.; Broomfield, L. M.; Martin, E.; Shafir, A. Hypervalent Activation as a Key Step for Dehydrogenative ortho C−C Coupling of Iodoarenes. *Chem. - Eur. J.* **2015**, *21*, 18779−18784. (g) Huang, X.; Zhang, Y.; Zhang, C.; Zhang, L.; Xu, Y.; Kong, L.; Wang, Z.-X.; Peng, Bo The ortho Difluoroalkylation of Aryliodanes with Enol Silyl Ethers: Rearrangement Enabled by a Fluorine Effect. *Angew. Chem., Int. Ed.* **2019**, *58*, 5956−5961. (h) Hyatt, I. F. D.; Dave, L.; David, N.; Kaur, K.; Medard, M.; Mowdawalla, C. Hypervalent Iodine Reactions Utilized in Carbon-carbon Bond Formations. *Org. Biomol. Chem.* **2019**, *17*, 7822−7848.
(5) (a) Ramtohul, Y. K.; Chartrand, A. Direct C-Arylation of β-Enamino Esters and Ketones with Arynes. *Org. Lett.* **2007**, *9*, 1029−1032. (b) Mohanan, K.; Coquerel, Y.; Rodriguez, J. Transition-Metal-free α-Arylation of β-Keto Amides via an Interrupted Insertion Reaction of Arynes. *Org. Lett.* **2012**, *14*, 4686−4689. (c) Chen, Q.; Zhang, C.; Chen, L.; Wen, C.; Du, Z.; Chen, H.; Zhang, H. α-Monoarylation and Tandem Arylation-insertion of Malonates with Arynes. *Tetrahedron Lett.* **2015**, *56*, 2094−2097. (d) Talero, A. G.; Martins, B. S.; Burtoloso, A. C. B. Coupling of Sulfoxonium Ylides with Arynes: A Direct Synthesis of Prochiral Aryl Ketosulfoxonium Ylides and Its Application in the Preparation of α-Aryl Ketones. *Org. Lett.* **2018**, *20*, 7206−7211. (e) Picazo, E.; Anthony, S. M.; Giroud, M.; Simon, A.; Miller, M. A.; Houk, K. N.; Garg, N. K. Arynes and Cyclic Alkynes as Synthetic Building Blocks for Stereodefined Quaternary Centers. *J. Am. Chem. Soc.* **2018**, *140*, 7605−7610.
(6) (a) Miyoshi, T.; Miyakawa, T.; Ueda, M.; Miyata, O. Nucleophilic α-Arylation and α-Alkylation of Ketones by Polarity Inversion of N-Alkoxyenamines: Entry to the Umpolung Reaction at the α-Carbon Position of Carbonyl Compounds. *Angew. Chem., Int. Ed.* **2011**, *50*, 928−931. (b) Miyoshi, T.; Sato, S.; Tanaka, H.; Hasegawa, C.; Ueda, M.; Miyata, O. One-pot Method for α-Phenylation of Ketones Using Isoxazolidine and Triphenylaluminum. *Tetrahedron Lett.* **2012**, *53*, 4188−4191. (c) Takeda, N.; Furuishi, M.; Nishijima, Y.; Futaki, E.; Ueda, M.; Shinada, T.; Miyata, O. Chiral Isoxazolidine-mediated Stereoselective Umpolung α-Phenylation of Methyl Ketones. *Org. Biomol. Chem.* **2018**, *16*, 8940−8943.
(7) (a) Kaiser, D.; de la Torre, A.; Shaaban, S.; Maulide, N. Metal-free Formal Oxidative C−C Coupling by In Situ Generation of an Enolonium Species. *Angew. Chem., Int. Ed.* **2017**, *56*, 5921−5925. (b) Maksymenko, S.; Parida, K. N.; Pathe, G. K.; More, A. A.; Lipisa, Y. B.; Szpilman, A. M. Transition-metal-free Intermolecular α-Arylation of Ketones via Enolonium Species. *Org. Lett.* **2017**, *19*, 6312−6315. (c) More, A. A.; Pathe, G. K.; Parida, K. N.; Maksymenko, S.; Lipisa, Y. B.; Szpilman, A. M. α-N-Heteroarylation and α-Azidation of Ketones via Enolonium Species. *J. Org. Chem.* **2018**, *83*, 2442−2447. (d) More, A. A.; Santra, S. K.; Szpilman, A. M. Azido-Enolonium Species in C−C and C−N Bond-Forming Coupling Reactions. *Org. Lett.* **2020**, *22*, 768−771.
(8) (a) Tang, Q.; Chen, X.; Tiwari, B.; Chi, R. Y. Addition of Indoles to Oxyallyl Cations for Facile Access to α-Indole Carbonyl Compounds. *Org. Lett.* **2012**, *14*, 1922−1925. (b) Vander Wal, M. N.; Dilger, A. K.; MacMillan, D. W. C. Development of a Generic Activation Mode: Nucleophilic α-Substitution of Ketones via Oxyallyl Cations. *Chem. Sci.* **2013**, *4*, 3075−3079. (c) Liu, C.; Oblak, E. Z.; Vander Wal, M. N.; Dilger, A. K.; Almstead, D. K.; MacMillan, D. W. C. Oxy-Allyl Cation Catalysis: An Enantioselective Electrophilic Activation Mode. *J. Am. Chem. Soc.* **2016**, *138*, 2134−2137. (d) Nguyen, T. N.; Setthakarn, K.; May, J. A. Oxyallyl Cation Capture via Electrophilic Deborylation of Organoboronates: Access to α,α′-Substituted Cyclic Ketones. *Org. Lett.* **2019**, *21*, 7837−7840. (e) Huang, W.-H.; Huang, G.-B.; Zhu, W.-R.; Weng, J.; Lu, G. Transition Metal-free Synthesis of α-Aryl Ketones via Oxyallyl Cation Capture with Arylboronic Acids. *Org. Chem. Front.* **2020**, *7*, 2480−2485. (f) Aota, Y.; Doko, Y.; Kano, T.; Maruoka, K. Bronsted Acid-Catalyzed Intramolecular α-Arylation of Ketones with Phenolic Nucleophiles via Oxy-Allyl Cation Intermediates. *Eur. J. Org. Chem.* **2020**, *2020*, 1907−1911.
(9) (a) Pichette Drapeau, M.; Fabre, I.; Grimaud, L.; Ciofini, I.; Ollevier, T.; Taillefer, M. Transition-metal-free α-Arylation of Enolizable Aryl Ketones and Mechanistic Evidence for a Radical Process. *Angew. Chem., Int. Ed.* **2015**, *54*, 10587−10591. (b) Pandey, G.; Tiwari, S. K.; Budakoti, A.; Sahani, P. K. Transition-metal-free Photoredox Intermolecular α-Arylation of Ketones. *Org. Chem. Front.* **2018**, *5*, 2610−2614.
(10) (a) Sousa e Silva, F. C.; Van, N. T.; Wengryniuk, S. E. Direct C−H α-Arylation of Enones with $ArI(O_2CR)_2$ Reagents. *J. Am. Chem. Soc.* **2020**, *142*, 64−69. (b) Porte, V.; Kaiser, D.; Maulide, N. Reductive Iodonium: Teaching an Old Claisen New Tricks. *Trends in Chemistry* **2020**, *2* (7), 589−592.
(11) Li, J.; Bauer, A.; Di Mauro, G.; Maulide, N. α-Arylation of Carbonyl Compounds through Oxidative C−C Bond Activation. *Angew. Chem., Int. Ed.* **2019**, *58*, 9816−9819.
(12) Bauer, A.; Di Mauro, G.; Li, J.; Maulide, N. An α-Cyclopropanation of Carbonyl Derivatives by Oxidative Umpolung. *Angew. Chem., Int. Ed.* **2020**, *59*, 18208−18212.
(13) (a) Zhdankin, V. V. Hypervalent Iodine(III) Reagents in Organic Synthesis. *ARKIVOC* **2009**, *2009*, 1−62. (b) Yoshimura, A.; Zhdankin, V. V. Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chem. Rev.* **2016**, *116*, 3328−3435. (c) Bauer, A.; Maulide, N. Recent Discoveries on the Structure of Iodine(III) Reagents and their Use in Cross-nucleophile Coupling. *Chem. Sci.* **2021**, *12*, 853−864.
(14) For a review on hypervalent iodine-mediated oxidative rearrangements see: (a) Singh, F. V.; Wirth, T. Oxidative Rearrangements with Hypervalent Iodine Reagents. *Synthesis* **2013**, *45*, 2499−2511. Selected applications using I(III): (b) Boye, A. C.; Meyer, D.; Ingison, C. K.; French, A. N.; Wirth, T. Novel Lactonization with Phenonium Ion Participation Induced by Hypervalent Iodine Reagents. *Org. Lett.* **2003**, *5*, 2157−2159. (c) Justik, M. W.; Koser, G. F. Oxidative Rearrangements of Arylalkenes with [hydroxy(tosyloxy)iodo]benzene in 95% Methanol: a General, Regiospecific Synthesis of α-Aryl ketones. *Tetrahedron Lett.* **2004**, *45*, 6159−6163. (d) Silva, L. F., Jr Hypervalent Iodine-mediated Ring Contraction Reactions. *Molecules* **2006**, *11*, 421−434. (e) Singh, F. V.; Rehbein, J.; Wirth, T. Facile Oxidative Rearrangements Using Hypervalent Iodine

https://dx.doi.org/10.1021/acs.orglett.1c00251
Org. Lett. 2021, 23, 2094−2098

Reagents. *ChemistryOpen* **2012**, *1*, 245−250. (f) Malmedy, F.; Wirth, T. Stereoselective Ketone Rearrangements with Hypervalent Iodine Reagents. *Chem. - Eur. J.* **2016**, *22*, 16072−16077. (g) Murai, K.; Kobayashi, T.; Miyoshi, M.; Fujioka, H. Oxidative Rearrangement of Secondary Amines Using Hypervalent Iodine(III) Reagent. *Org. Lett.* **2018**, *20*, 2333−2337. (h) Sun, Y.; Huang, X.; Li, X.; Luo, F.; Zhang, L.; Chen, M.; Zheng, S.; Peng, B. Mild Ring Contractions of Cyclobutanols to Cyclopropyl Ketones via Hypervalent Iodine Oxidation. *Adv. Synth. Catal.* **2018**, *360*, 1082−1087.

(15) Arava, S.; Santra, S. K.; Pathe, G. K.; Kapanaiah, R.; Szpilman, A. M. Direct Umpolung Morita−Baylis−Hillman like α-Functionalization of Enones via Enolonium Species. *Angew. Chem., Int. Ed.* **2020**, *59*, 15171−15175.

(16) Yield determined by NMR analysis, using mesitylene as an internal standard. The products were not isolated due to a tendency towards polymerization, in particular, for **7o**, and comparable volatility. On the basis of literature precedent, we do not anticipate this to be a general problem for alkyl-substituted enones: Harada, S.; Matsuda, D.; Morikawa, T.; Nishida, A. Direct Synthesis of Enones by Visible-Light-Promoted Oxygenation of Trisubstituted Ole-fins Using Molecular Oxygen. *Synlett* **2020**, *31*, 1372−1377.

https://dx.doi.org/10.1021/acs.orglett.1c00251
Org. Lett. 2021, 23, 2094−2098