



OPEN ACCESS

EDITED AND REVIEWED BY
Iwao Ojima,
Stony Brook University, United States

*CORRESPONDENCE

Toshifumi Dohi,
td1203@ph.ritsumeikai.ac.jp
Jian-Wei Han,
jianweihan@ecust.edu.cn
Ravi Kumar,
ravi.dhamija@rediffmail.com

SPECIALTY SECTION

This article was submitted to Organic Chemistry, a section of the journal Frontiers in Chemistry

RECEIVED 16 July 2022

ACCEPTED 25 July 2022

PUBLISHED 05 September 2022

CITATION

Dohi T, Han J-W and Kumar R (2022), Editorial: New hypervalent iodine reagents for oxidative coupling—volume II. *Front. Chem.* 10:995702. doi: 10.3389/fchem.2022.995702

COPYRIGHT

© 2022 Dohi, Han and Kumar. This is an open-access article distributed under the terms of the [Creative Commons Attribution License \(CC BY\)](https://creativecommons.org/licenses/by/4.0/). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

Editorial: New hypervalent iodine reagents for oxidative coupling—volume II

Toshifumi Dohi^{1*}, Jian-Wei Han^{2*} and Ravi Kumar^{3*}

¹College of Pharmaceutical Sciences, Ritsumeikan University, Shiga, Japan, ²School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, China, ³Department of Chemistry, J. C. Bose University of Science and Technology, YMCA, Faridabad, India

KEYWORDS

hypervalent compounds, iodine, reagent, oxidative coupling, synthetic application

Editorial on the Research Topic

New hypervalent iodine reagents for oxidative coupling - volume II

Hypervalent iodine compounds (HICs), of which iodine is in high oxidation states (+3 or +5), have aroused widespread interest in the fields of synthetic chemistry, and they are valuable as versatile reagents in organic chemistry. Specifically, efficient syntheses make the hypervalent iodine reagents (HIRs) all more practical and environmentally benign.

Historically, the early HICs date back to the 1880–1890s, when Willgerodt prepared (dichloroiodo)benzene as the first HIC, followed by the discovery of (diacetoxyiodo)benzene, iodosylbenzene, 2-iodoxybenzoic acid (IBX) and diaryliodonium salts successively. These early HICs are very useful reagents that we still frequently use in organic synthesis nowadays. With these structurally diversified HICs in hand, the synthetic utilization of them opened up new synthetic pathways, and then have achieved considerable attention. During the long history of research, exploration of diversification of structures and reactivity with hypervalent iodine chemistry has already led to many useful methodologies for modern organic synthesis. Particularly, the unique reactivity pattern of HIRs is similar to that of the transition-metal species, and the reactions of HIRs are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination, ligand coupling and even the radical process, which represents the most important hotspot in current organic chemistry. Therefore, renewed interest in recent years on the hypervalent reagents is leading to a boom in new synthetic methodologies, mechanistic understandings, potential applications in bioactive molecules.

Last year in 2021, Toshifumi Dohi (Ritsumeikan University, Japan), Jian-Wei Han (East China University of Science and Technology, China) and Ravi Kumar (J.C. Bose University of Science and Technology, India) have organized a Topic issue of Frontiers in Chemistry that includes 10 articles covering key topics of hypervalent iodine chemistry. The issue was successful to reach 37,044 views so far. Considering the explosive accomplishment in organoiodine chemistry, the managing editor requested to

organize the second issue on this topic. We therefore embarked on this Research Topic collection titled “New Hypervalent Iodine Reagents for Oxidative Coupling -Volume II”. It is hoped that the collective efforts of the authors of these articles will serve to broaden the foundation that supports future growth in hypervalent iodine chemistry and the influx of new ideas that growth brings. The articles that make up this topic are contributed by authors from the international community, showcasing the widespread adoption of HICs and their continuous development in synthetic organic chemistry. We introduce the key articles below.

Utilization of HICs and iodine as a versatile combination to produce *O*-radicals from different substrates, such as, alcohols, acetals, and acids is explored in literature. These initially generated *O*-radicals are reported to undergo β -scission giving rise to *C*-radicals that readily gets oxidized to cationic intermediates. Cationic intermediates, thus formed, can be easily attacked by diverse nucleophiles that give an excellent metal-free synthetic protocol to access various bioactive or potential bioactive targets. Boto et al. presented a selection of one-pot scission-oxidation-addition of *C*, *N*, and *P* nucleophiles involving scission-alkylation, scission-arylation, fragmentation-Diels Alder and other inter- and intramolecular cyclization processes, scission-Ritter, fragmentation-addition of nucleobases, and scission-phosphorylation. The majority of the substrates discussed by the group are amino acids, β -hydroxy amines or carbohydrates.

HICs have emerged as resourceful environmentally benign alternatives to heavy-metal oxidants. However, the common preparation methods of HIRs often require hazardous or expensive oxidants. Hence, direct and sustainable methods for their preparation are always in demand. Recently, many researchers have started exploiting the use of electrochemical oxidation for the preparation of HIRs via the anodic oxidation of iodine(I) precursors. Several oxidative transformations have been successfully achieved by using *in situ* electrogenerated HIRs as reviewed recently by Francke and Wirth research groups (Francke et al., 2018; lsherbini and Wirth, 2018; Francke, 2019; Francke, 2021). Chen and Yang presented an overview of the recent advances in this area during the past 3 years. This minireview encompasses the recent developments of electrochemical synthesis of HIRs and, applications of *in-situ* electrochemically generated HIRs as redox mediators in organic electrochemistry.

Direct or late-stage incorporation of thio/selenocyanato functional groups is of utmost importance as evident from huge biological applications bearing these moieties. In this regard, Du et al. reported an excellent example of a metal-free hypervalent iodine-mediated electrophilic thio/selenocyanation approach for the construction of functionalized isocoumarin frameworks. The group

successfully achieved the synthesis of C4-thio/selenocyanated isocoumarins *via* thio/selenocyanation of alkynes using PhICl_2 and $\text{NH}_4\text{SCN}/\text{KSeCN}$ reagents. The developed protocol involves the thio/selenocyanation, enabled by thio/selenocyanogen chloride generated *in-situ*, followed by an intramolecular lactonization. A Gram scale synthesis of xyridin A and antitumor activity of the synthesized compounds are also presented.

Another example of hypervalent iodine-mediated alkyne functionalization was presented by Liu et al., in which the group reported chemoselective halogenation of terminal alkynes. The terminal alkynes have been reported to give mono-bromination (1-bromoalkynes), di-bromination (1,2-dibromoalkenes) and, tetra-bromination (1,1,2,2-tetrabromoalkanes) of terminal alkynes using TBAB/PIDA, NaBr/PIDA and NaBr/PIDA (in excess), respectively. A certain amount of water with NaBr/PIDA system changes the dibromination product formation to α,α -dibromoketones.

Liu et al. reported mechanism-dependent selectivity in fluorocyclization of unsaturated carboxylic acids or alcohols by hypervalent iodine. Density functional theory (DFT) studies were performed to understand the unprecedented difference between 6-*endo* and 5-*exo* selectivity in hypervalent iodine(III)-promoted fluorocyclization of unsaturated carboxylic acids or alcohols by difluoroiodotoluene. The research provides insights into the mechanism-dependent selectivity should help advance the development of fluorocyclization reactions with HIRs.

HICs have evolved as mainstream reagents particularly due to their excellent oxidizing ability, high electrophilicity and versatile reactivity. Singh et al. summarized the recent advances in non-palladium catalyzed oxidative coupling reactions using HIRs. This review article critically summarizes the recent developments in non-palladium-catalyzed oxidative coupling reactions mediated by HIRs with great emphasis on understanding the mechanistic aspects in detail.

Goreshnik et al. described oxidation of iodine to dihaloiodate(I) salts of amines with hydrogen peroxides and their crystal structures. In this research article, the authors report a general preparation of dihaloiodate salts of heterocyclic amines (tertiary and quaternary) and their structure was determined by NMR and Raman spectroscopy and single crystal X-ray diffraction.

This collection of articles showcases different aspects of hypervalent iodine compounds towards achieving various valuable organic transformations. Irrespective of the fact that there are continuous expansions in this field, there are still many areas yet to be explored. By taking into account the advantages of hypervalent iodine-mediated oxidative coupling reactions, it seems certain that these reactions will be further utilized in the development of sustainable synthetic methods.

Author contributions

All authors provided comments and discussed the contents, and approved this Editorial for publication.

Acknowledgments

We would like to express our sincere gratitude to all authors for their valuable contributions to this special thematic issue. We also thank the reviewers for their voluntary work in evaluating the submitted articles and for constructive advice on the improvement of the quality. We would also like to thank the Specialty Chief Editor Iwao Ojima, and other editorial board members of the organic chemistry section for their continuous cooperation in preparing this Special Issue.

References

Francke, R., Broese, T., and Roesel, A. F. (2018). "Electrochemistry of hypervalent iodine compounds," in *Hypervalent halogen compounds*. Editor I. Marek (John Wiley & Sons), 1–22. doi:10.1002/9780470682531.pat0960

Francke, R. (2019). Electrogenerated hypervalent iodine compounds as mediators in organic synthesis. *Curr. Opin. Electrochem.* 15, 83–88. doi:10.1016/j.coelec.2019.03.012

Francke, R. (2021). Recent progress in the electrochemistry of hypervalent iodine compounds. *Curr. Opin. Electrochem.* 28, 100719. doi:10.1016/j.coelec.2021.100719

Kikushima, K., Elboray, E. E., Jiménez-Halla, J. O. C., Solorio-Alvarado, C. R., and Dohi, T. (2022). Diaryliodonium(III) salts in one-pot double functionalization of

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

C–I(III) and ortho C–H bonds. *Org. Biomol. Chem.* 20, 3231–3248. doi:10.1039/D1OB02501E

Isherbini, M., and Wirth, T. (2018). Hypervalent iodine reagents by anodic oxidation: A powerful green synthesis. *Chem. Eur. J.* 24, 13399–13407. doi:10.1002/chem.201801232

Wang, Y., An, G., Wang, L., and Han, J. (2020). Diaryliodonium salts: Structures and synthesis. *Curr. Org. Chem.* 24, 2070–2105. doi:10.2174/1385272824999200507124328

Yoshimura, A., and Zhdankin, V. V. (2016). Advances in synthetic applications of hypervalent iodine compounds. *Chem. Rev.* 116, 3328–3435. doi:10.1021/acs.chemrev.5b00547