Eietsu HASEGAWA, Dr. Sci.

Professor
Program: Fundamental Sciences
Area: Chemistry
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Professional Expertise

Organic Chemistry, particularly focused on the mechanism and synthetic application of
1) electron transfer reactions, 2) photo-promoted reactions, 3) free radical reactions, and their green-sustainable aspects.

Research Fields of Interest

Photoinduced electron transfer (PET) reaction of organic compounds

- PET promoted reductive transformations of carbonyl compounds and halides utilizing N-heterocyclic electron donors, such as 1,3-dimethyl-2-phenyl benzimidazoline and its derivatives, are investigated. In the oxidative transformation event, PET promoted regioselective ring-opening reaction of bicyclic cyclopropyl silyl ethers was developed.

Thermal transformation of organic compounds promoted by redox reagents

- Samarium diiodide promoted reductions of carbonyl substrates and halides are studied. In these reactions, intramolecular reactivity of samarium ketyl radicals with other functional groups, such as carbon-halogen bonds and ester carbonyls, is particular interest. Also, oxidative ET reaction of certain cyclopropanol derivatives promoted by Fe (III), Ce (IV), Mn (III) salts and amine radical cation salt is investigated.

Green and sustainable electron transfer (ET) chemistry and radical chemistry

- Development of environmentally benign ET methods to achieve organic transformations is our recent interest. For this objective, improvement of the efficiency as well as the selectivity of above described reactions is required. Also, discovery of effective ET reactions using environmentally benign solvents such as ionic liquids, fluorine containing organic solvents is interesting. In addition, development of free radical reactions without organotin hydrides and benzene is investigated. Recently, benzotrifluoride was found to be an effective solvent both for free radical reactions using an organosilicon hydride and for various electron-transfer reactions.

Education

1985: Dr. Sci. in Chemistry, Graduate School of Science, Tohoku University, Japan
1982: M.Sci. in Chemistry, Graduate School of Science, Tohoku University, Japan
1980: B.Sci. in Chemistry, Faculty of Science, Yamagata University, Japan

Professional Societies and Activities

1. The Chemical Society of Japan
   Associate Editor of Bulletin of the Chemical Society of Japan
2. The Society of Synthetic Organic Chemistry, Japan
3. The Japanese Photochemistry Association
4. American Chemical Society

Major Publications

Original Papers

[1] "A photo-reagent system of benzimidazoline and $Ru(bpy)_3Cl_2$ to promote hexenyl radical cyclization and Dowd-Beckwith ring-expansion of alpha-halomethyl substituted benzocyclic-1-alkanones", E. Hasegawa, M. Tateyama, T. Hoshi, T. Ohta, E. Tayama, H. Iwamoto, S. Takizawa, S. Murata, *Tetrahedron*, 70, 2776-2783, 2014

[2] "Carbon-carbon bond formation via benzoyl umpolung attained by photoinduced electron-transfer with benzimidazolines", T. Igarashi, E. Tayama, H. Iwamoto, E. Hasegawa, *Tetrahedron Lett.,* 54, 6874-6877, 2013

[3] "Copper (II) salt promoted oxidative ring-opening reactions of bicyclic cyclopropanol derivatives via radical pathways", E. Hasegawa, M. Tateyama, R. Nagumo, E. Tayama, H. Iwamoto, *Beilstein J. Org. Chem. (Thematic Series. Organic Free Radical Chemistry),* 9, 1397-1406, 2013

[4] "Photoinduced Electron-transfer Reaction of alpha-Bromomethyl-substituted Benzocyclic beta-Keto Esters with Amines: Selective Reaction Pathways Depending on the Nature of Amine Radical Cations", E. Hasegawa, E. Tosaka, A. Yoneoka, Y. Tamura, S. Takizawa, M. Tomura, Y. Yamashita, *Res. Chem. Intermed.,* 39, 247-267, 2013

[5] "An effective procedure to promote aza–Prins cyclization reactions employing a combination of ferric chloride and an imidazolium salt in benzotrifluoride", C. Osawa, M. Tateyama, K. Miura, E. Tayama, H. Iwamoto, E. Hasegawa, *Heterocycles,* 86, 1211-1226, 2012

[6] "Application of biphasic reaction procedure using ferric chloride dissolved in an imidazolium salt and benzotrifluoride (FeIm-BTF procedure) to aza-Prins cyclization reaction", E. Hasegawa, N. Hiroi, C. Osawa, E. Tayama, H. Iwamoto, *Tetrahedron Lett.,* 51, 6535-6538, 2010

[7] "Novel biphasic reaction system of ferric chloride dissolved imidazolium hexafluorophosphate and benzotrifluoride: application to electron transfer reaction of cyclopropyl silyl ethers", H. Tsuchida, E. Hasegawa, *Tetrahedron*, 66*,* 3447-3451, 2010

[8] "In situ generated tris(*p*-bromophenyl)amine radical cation promoted electron transfer reaction of cyclopropyl silyl ethers" E. Hasegawa, K. Kakinuma, T. Yanaki, S. Komata, *Tetrahedron (Symposium-in-Print. Electrontransfer reagents in organic synthesis),* 65*,* 10876-10881, 2009

[9] "Cyclization and ring-expansion processes involving samarium diiodide promoted reductive formation and subsequent oxidative ring-opening of cyclopropanol derivatives" H. Tsuchida, M. Tamura, E. Hasegawa, *J. Org. Chem.,* 74, 2467-2475, 2009

[10] "Benzimidazoline-dimethoxypyrene. An effective promoter system for photoinduced electron transfer promoted reductive transformations of organic compounds" E. Hasegawa, H. Hirose, K. Sasaki, S. Takizawa, T. Seida, N. Chiba, *Heterocycles*, 77, 1147-1161, 2009

[11] "Tris(trimethylsilyl)silane promoted radical reaction and electron-transfer reaction in benzotrifluoride" E. Hasegawa, Y. Ogawa, K. Kakinuma, H. Tsuchida, E. Tosaka, S. Takizawa, H. Muraoka, T. Saikawa, *Tetrahedron, 64,* 7724-7728, 2008

[12] "Electron transfer promoted regioselective ring-opening reaction of cyclopropyl silyl ethers" E. Hasegawa, N. Yamaguchi, H. Muraoka, H. Tsuchida, *Org. Lett.*, 9, 2811-2814, 2007

[13] "The first example of samarium diiodide-promoted intramolecular ketone–ester coupling of ketones tethering acyloxyalkyl side chains producing 2-hydroxy cyclic hemiacetals" E. Hasegawa, K. Okamoto, N. Tanikawa, M. Nakamura, K. Iwaya, T. Hoshi, T. Suzuki, *Tetrahedron Lett.*, 47, 7715-7718, 2006

[14] "Photoinduced electron transfer systems consisting of electron-donating pyrenes or anthracenes and benzimidazolines for reductive transformation of carbonyl compounds" E. Hasegawa, S. Takizawa, T. Seida, A. Yamaguchi, N. Yamaguchi, N. Chiba, T. Takahashi, H. Ikeda, K. Akiyama, *Tetrahedron (Symposium-in-Print. The chemistry of radical ions)*, 62, 6581-6588, 2006

[15] "Cyclization and ring-expansion reactions involving reductive formation and oxidative ring-opening of cyclopropanol derivatives" E. Hasegawa, H. Tsuchida, M. Tamura, *Chem. Lett.*, 34, 1688-1689, 2005

[16] "Contrastive photoreduction pathways of benzophenones governed by regiospecific deprotonation of imidazoline radical cations and additive effects" E. Hasegawa, T. Seida, N. Chiba, T. Takahashi, H. Ikeda, *J. Org. Chem.*, 70, 9632-9635, 2005

[17] "2-Hydroxyphenyl-1,3-dimethylbenzimidazolines. Formal two hydrogen atom-donors for photoinduced electron transfer reactions", E. Hasegawa, N. Chiba, T. Takahashi, S. Takizawa, T. Kitayama, T. Suzuki, *Chem Lett.*, 33, 18-19, 2004

[18] "Novel transformation of 2-substituted alkyl 1-indanone-2-acetates to 6-substituted 3,4-benzotropolones through sequential reduction and oxidation processes using Sm(II) and Ce(IV) Salts", K. Iwaya, M. Tamura, M. Nakamura, E. Hasegawa, *Tetrahedron Lett.*, 44, 9317-9320, 2003

Reviews and Book Chapters

[1] "Application of Photoinduced Electron Transfer (PET) Reactions to Organic Synthesis–Recent examples utilizing photosensitization procedures–", Eietsu Hasegawa, Photochemistry *Photochemistry*, 41, 40-44 (Japanese), 2010

[2] E. Hasegawa, M. Kamata, "Photoinduced Electron Transfer Reactions of Oxiranes and Epoxy Ketones", in *CRC Handbook of Organic Photochemistry and Photobiology,* Horspool, W. M. and Lenci, F., Eds., CRC Press, Boca Raton, Chapter 53, 1-17, 2004

[3] E. Hasegawa, "Characteristic Reactivities of Some Rearrangeable Ketyl Radicals Generated through Photoinduced Electron Transfer Processes", *J. Photoscience*, 10, 61-69, 2003

[4] E. Hasegawa, "Organic Synthesis Utilizing Photoinduced Electron Transfer (PET) Reactions -Are PET Reactions Attractive to Synthetic Organic Chemistry?-", *Photochemistry,* 33, 220-222 (Japanese), 2002