Tetrahedron 66 (2010) 5737–5738

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Preface

Hypervalent iodine chemistry—recent advances and applications

Discoveries in science and in chemistry have often remained for a long time reduced to mere scientific curiosities before constituting the bases of the development of a dedicated domain of research investigations. The study of the chemistry of hypervalent iodine compounds undeniably belongs to this category of topics in the chemical sciences. Since the first preparation of a hypervalent iodine compound, the λ^3-iodane $PhCl_2$, reported by the German chemist Conrad Willgerodt in 1886, research activities on hypervalent iodine chemistry have gone through ups and downs in terms of intensity worldwide and remarkability of the results. Despite a comprehensive book by Willgerodt in 1914 on this chemistry, only since the late sixties, the quality of the research on hypervalent iodine chemistry, and in particular, on the development of new iodanes, their utilisation as mild and versatile reagents in organic chemistry, the description of their mechanistic implications, and their diverses applications in organic synthesis of complex molecular architectures, has gradually improved. Since the last fifteen years or so, the field is even undergoing a new and still growing burst of interest, as it can be inferred from the increasing numbers of reports on the total synthesis of complex natural products relying on the use of hypervalent iodine reagents in key steps, on new developments of the use of chiral iodane variants for asymmetric synthesis, including organoiodine-catalyzed systems, and on still novel exploitations of iodanes as reagents capable of mediating diverse C—C, C—O, C—N and C—Halogen bond-forming transformations. Last, but not least, an increasing number of chemists are realizing that the use of hypervalent iodine reagents constitutes an environmentally friendly alternative to that of heavy and toxic metal-based reagents for mediating numerous and valuable reactions originally developed within the field of organometallic chemistry. This added value of the chemistry of hypervalent iodine compounds is certainly also one of the factors, that is, today inciting more chemists to work with such reagents and to develop novel variants in these years of concerns for the protection of the environment and for the development of a 'greener' and sustained organic chemistry.

The project of the publication of this Symposium-in-Print dedicated to the recent advances and applications of hypervalent iodine chemistry has been initiated in concert with the organization of the third International Conference on Hypervalent Iodine Chemistry (ICHCI2010), which took place at the European Institute of Chemistry and Biology on the University of Bordeaux campus, in Pessac, France, from July 4 to July 7, 2010. In agreement with Prof. Léon Ghosez, Editor-in-Chief of the Tetrahedron Symposium-in-Print series, we invited the plenary and invited lecturers of this conference to contribute to this publication project. Most of them have responded positively, together with other researchers active in the field, who we also invited to contribute. Their articles conveying accounts of their recent research and/or unveiling new results are thus compiled herein.

Organizer of the two previous editions of the ICHIC in Greece (Kallithea in 2001, and Thessaloniki in 2006), Anastasios Varvoglis, now retired from the Aristotle University of Thessaloniki, kindly accepted to write a commentary on the history of the development of hypervalent iodine chemistry. This is reminding us of some significant contributions by many pioneers in the field, notably those of the Russian school, whose major work was unfortunately too often published only in Russian.

The first research report of this Symposium-in-Print is by Viktor Zhdankin and Victor Nemykin from the University of Minnesota Duluth and their Russian colleague Mekhman Yusubov from The Siberian State Medical University and Tomsk Polytechnic University, and concerns the use of hypervalent iodine species in transition metal-mediated dehydrogenative and oxygenative catalytic oxidation reactions. Antonio Togni and co-workers at the ETH Zürich report on the synthesis, structure, and reactivity of new hypervalent iodine reagents for electrophilic trifluoromethylation reactions. Hermann-Josef Frohn and colleagues from the Universities of Duisburg-Essen and Paderborn present their approach to the preparation of unusual fluorophenyl(pentafluorophenyl) difluoroiodonium(V) tetrafluoroborate salts and discuss their properties as fluoro-oxidizers. John Protasiewicz and Bindu Meprathu at the Case Western Reserve University in Cleveland, USA, describe the synthesis and characterization of new hypervalent *ortho*-sulfonyl iodine reagents with enhanced solubility in organic solvents, such as chloroform. Yasuyuki Kita and associates now at the Ritsumeikan University in Japan (formerly at Osaka University) report on the versatility of fluoroalcohols as solvents in hypervalent iodine chemistry, with a focus on their utility for the synthesis of diaryliodinium(III) salts. Novel chiral diaryliodonium(III) salts have been designed and synthesized by Berit Olofsson and Nazali Jalalian from Stockholm University, as described in their contribution for this issue. Spyros Spyroudis, Elizabeth Malamidou-Xenikaki and their colleagues at the Aristotle University of Thessaloniki describe the trifluoroboron-mediated arylation of the lawsone-derived phenyliodonium ylide with electron-rich arenes without relying on the use of any metal catalyst, as well as with aromatic aldehydes in an interesting deformylation context. Robert Moriarty and co-workers at the University of Illinois at Chicago report remarkable metal-free intramolecular cyclopropanation reactions of olefins through the use of iodonium ylide species. Imanol Tellitu and colleagues at the Universidad del País Vasco in Leioa, Spain, describe the use of the λ^3-iodane bis(trifluoroacetoxy)iodobenzene reagent in the conversion of alkynylamides into structurally diverse pyrrolo(benzo) diazepine derivatives. Masahito Ochiai and co-workers at the University of Tokushima investigated the effects of stereochemistry

doi:10.1016/j.tet.2010.06.026

and β-substitution on the rates of the vinylic S_N2 reaction of hypervalent vinyl(phenyl)-λ^3-iodanes with tetrabutyl-ammonium halides. A survey of the recent literature in the field indicates that phenols have emerged as privileged substrates in current developments of hypervalent iodine chemistry. This tendency is herein confirmed by several reports. Om Prakash and collaborators at the Kurukshetra University in Haryana, India, revisited the versatility of hydroxy(tosyloxy)iodobenzene (Koser's reagent) for the tosylation of phenols. Takayuki Yakura and colleagues at the University of Toyama report dearomatizing oxygenation reactions of phenols into *para*-quinols or *para*-quinones using a catalytic amount of 4-iodophenoxyacetic acid and oxone as a terminal oxidant. Kazuaki Ishihara and co-workers at Nagoya University describe the design and performances of their conformationally flexible C_2-symmetric chiral λ^3-iodane catalyst in enantioselective Kita oxidative (dearomatizing) spirolactonization of 1-naphthol derivatives, followed by diasteroselective epoxidation. Hypervalent iodine-mediated phenol dearomatization processes have found many applications in the synthesis of complex natural product synthesis. Examples are provided in several articles of this Symposium-in-Print. Peter Wipf's group describes the transformation of simple arenols into analogues of functionalized bicyclo[3.3.1]non-3-en-2-ones motifs featured in the natural products gymnastatins F and Q. Yung-Sing Wong and colleagues at the University of Grenoble, France, report some elegant λ^3-iodane-mediated tandem oxidative reactions for the synthesis of bioactive polyspirocyclohexa-2,5-dienone analogues of the antimalarial aculeatins. Thomas Pettus' group at the University of California, Santa Barbara, offers us a detailed account of the various facets of the chemistry they encountered when working with chiral cyclohexadienones derived from λ^3-iodane-mediated dearomatization of chiral resorcinol derivatives. Marco Ciufolini and Huan Liang at The University of British Columbia, Canada, discuss the oxidative dearomatizing amidation of phenols and its various applications in the synthesis of selected alkaloids. Sylvain Canesi and co-workers at the Université du Québec à Montréal give us an account of their work on λ^3-iodane-mediated umpolung activation of phenols for the construction of various natural product cores.

Finally, we both took the liberty of contributing to this Symposium-in-Print with an article by Altermann et al. on the synthesis and application of new chiral λ^5-iodanes as stoichiometric oxidants and an article by Pouységu et al. on the use of λ^3- and λ^5-iodanes in stereo- and chemoselective oxygenative phenol dearomatization reactions.

We hope that you will appreciate reading this collection of articles that should give you a decent, albeit non-exhaustive, overview of the current state-of-the-art in hypervalent iodine chemistry. Further valuable applications of hypervalent iodine compounds in organic synthesis surely still await around the corner, and the remaining challenges in the development of their exploitation in asymmetric synthesis will certainly be met in the near future, so keep an eye on the literature for new and exciting results.

We would like to express our sincere thanks and congratulations to all of the contributors who participated in this enterprise.

Stéphane Quideau
Université de Bordeaux, Président du Groupe Polyphénols, Institut des Sciences Moléculaires (CNRS-UMR 5255), Institut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607 Pessac Cedex, France
E-mail address: s.quideau@iecb.u-bordeaux.fr

Thomas Wirth
Cardiff University, Cardiff School of Chemistry, Park Place, Main Building, Cardiff CF10 3AT, Wales, UK
E-mail address: wirth@cf.ac.uk