Synthesis of Functionalized Iodoarenes by Iododecarboxylation of Aromatic Carboxylic Acids

Biography

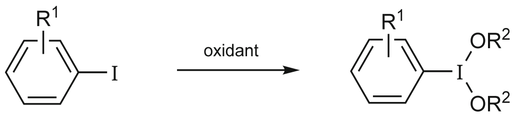
Fateh Veer Singh is currently Assistant Professor in Chemistry at VIT University in Chennai, India. He completed his PhD in 2007 with Dr Atul Goel (CDRI, Lucknow, India). After completion of his doctoral studies, he was involved in postdoctoral studies for six years in three different research groups (Prof. H A Stefani at USP, São Paulo, Brazil; Prof. Thomas Wirth at Cardiff University, UK; and Prof. G Mugesh at IISc Bangalore, India). During his postdoctoral studies, his stay as Marie Curie postdoctoral fellow with Prof. Wirth was most fruitful as he gained a valuable research experience in the area of organoselenium and hypervalent iodine chemistry. He joined his current position at VIT University, Chennai in 2014. Currently, he is working on various oxidative transformations with iodine(III) reagents including catalysis.

Institution

VIT University, Chennai Campus, Chennai

Abstract

Our research group is currently involved in the synthesis of new hypervalent iodine reagents and their applications in organic synthesis. These reagents have received particular attention due to their oxidation properties, mild reaction conditions, and environmentally friendly nature. Generally, hypervalent iodine reagents exist in the form of iodine(III) and iodine(V) reagents. In our on-going research project, we are aiming to synthesize novel iodine(III) reagents 2 by the oxidation of iodoarenes 1 (Scheme 1). In order to synthesize the iodoarenes, *Science of Synthesis* Online was used as a tool for literature search. Performing a literature search using this tool, we were able to find an excellent method for the synthesis of iodoarenes.



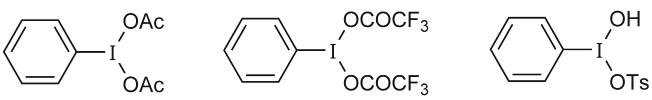
1 **2**

R^1 = EDG or EWG: R^2 = Ac, $COCF_3$

Scheme 1 Synthesis of Iodine(III) Reagents by Oxidation of Iodoarenes

Discussion

Various iodine(III) reagents are already reported in the literature and leading reagents are (diacetoxyiodo)benzene (**3**, PIDA), [bis(trifluoroacetoxy)iodo]benzene (**4**, PIFA), and [hydroxy(tosyloxy)iodo]benzene (**5**, Koser's reagent) (Scheme 2). Our target was to synthesize novel iodine(III) reagents having electron-withdrawing and electron-donating substituents on the phenyl ring and observe the influence of these groups on their electrophilic properties during the cyclization of ortho-functionalized stilbenes.

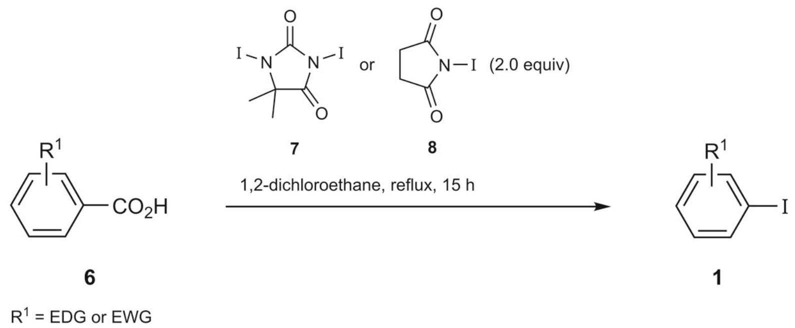


3 **4** **5**

Scheme 2 Structures of Existing Iodine(III) Reagents

Contact
Science of Synthesis Editorial Office • Georg Thieme Verlag KG • Ruedigerstrasse 14 • 70469 Stuttgart • Germany

Initially, (diacetoxyiodo)benzene (**3**) and [bis(trifluoroacetoxy)iodo]benzene (**4**) were synthesized by the oxidation of iodobenzene using hydrogen peroxide and Oxone as oxidants, respectively. Subsequently, we directed our efforts towards the synthesis of new iodine(III) reagents. Although, some functionalized iodobenzenes are commercially available, most of them were quite expensive and difficult to purchase. A few attempts were made to synthesize functionalized iodoarenes but most of them were associated with poor yields. We then searched the literature using *Science of Synthesis* Online and found an excellent chapter on the synthesis of iodoalkanes by the substitution of carbon functionalities (Section 35.3.1.3.8) published in *Science of Synthesis*, Knowledge Updates 2015/2 written by Elliott and Saleh and edited by Prof. Thomas Wirth. In this chapter, several methods for the iodination of both aliphatic and aromatic species were discussed. In one method, the synthesis of iodoarenes **1** was achieved by iododecarboxylation of benzoic acids **6** using 1,3-diiodo-5,5-dimethylhydantoin (**7**, DIH) or *N*-iodosuccinimide (**8**, NIS) as iodine source (Scheme 3).



Scheme 3 Synthesis of Iodoarenes by Iododecarboxylation of Benzoic Acids Using *N*-Iodosuccinimide or 1,3-Diiodo-5,5-dimethylhydantoin as Iodine Source.

In our research studies, this process was used for the synthesis of various iodoarenes **1** functionalized with both electron-withdrawing and electron-donating functionalities. Various benzoic acids substituted with electron-withdrawing groups were successfully used as substrates and iodoarenes **1** were isolated in excellent yield. Although, the same reaction was useful for the synthesis of iodoarenes **1** functionalized with electron-donating groups the reaction products were isolated in poor yield. 1,3-Diiodo-5,5-dimethylhydantoin (**7**) and *N*-iodosuccinimide (**8**) were used as iodine source and both are commercially available. Subsequently, the synthesized iodoarenes **1** were oxidized to the corresponding iodine(III) reagents **2** using Oxone and hydrogen peroxide as oxidants (Scheme 1). Comparative studies of the electrophilic behavior of these the synthesized reagents **2** in cyclization reactions is currently work in progress.

Conclusion

Science of Synthesis Online is an important search tool for synthetic organic chemists. It is easily accessible and quite easy to search the literature using this tool. Review articles published in *Science of Synthesis* Online provide important information such as the safety profile of reagents used and general experimental procedures. The study of this resource provides a great opportunity to learn more about various aspects of research, especially for inexperienced research students. *Science of Synthesis* Online proved immensely useful during our synthesis of functionalized iodine(III) reagents. We are close to completing our research project due to the synthetic routes we found in *Science of Synthesis* Online.