

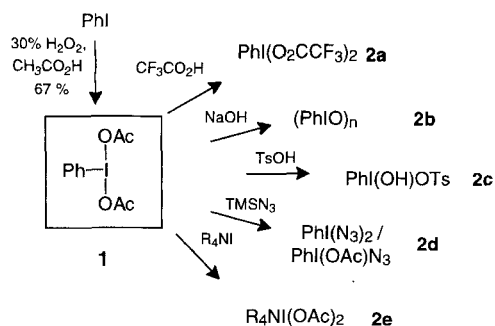
**(Diacetoxyiodo)benzene DIB – a Multitalented Oxidant in Organic Synthesis**

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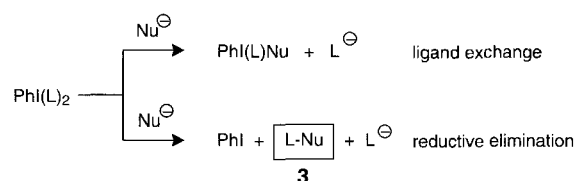
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Organic compounds of polycoordinated iodine have long been known. In fact, in 1886 Willgerodt [1] presented the first preparation of  $\text{PhICl}_2$  from iodobenzene and  $\text{ICl}_3$  in this journal! Only recently iodine compounds in the oxidation state III have gained synthetic and mechanistic significance, as described in numerous recent reviews [2]. This renewed interest was initiated by the development of various new iodine(III) reagents **2a–d** as well as iodate(I) salts **2e** which in most cases can conveniently be prepared *in situ* from a common iodine(III) precursor, *i. e.* (diacetoxyiodo)benzene DIB (**1**) (Scheme 1) [3].



Scheme 1

The strongly electrophilic character of hypervalent iodine is mainly responsible for its diverse chemistry. The reactivity pattern of **1** and other iodine(III) reagents is briefly summarized in Scheme 2. It is primarily based on ligand exchange reactions and reductive elimination of two ligands on the central iodine atom. In most cases, reactions of **1** with nucleophiles are terminated by the second route, affording final products **3** with a combination of L and Nu. Due to this behaviour compounds like **1** are occasionally termed “nonorganometallic” reagents.



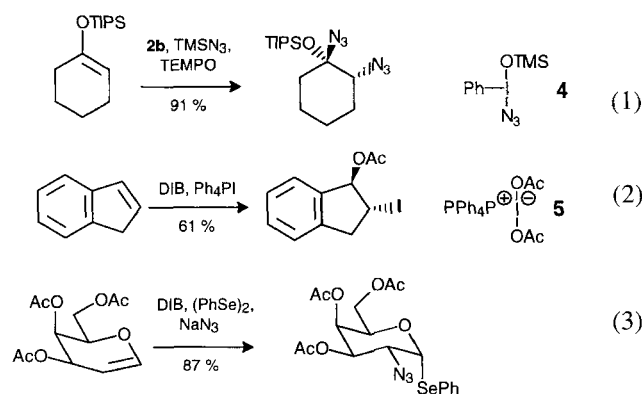
Scheme 2

As will be shown, the breaking of the I–L bond can occur hetero- or homolytically.

For successfully introducing a new reagent or reaction on the “market” of preparative organic chemistry today, it is important that the conversion described is highly stereo-, regio- and as has often be forgotten chemospecific. Unfortunately, most reviews on iodine(III) [2] have not addressed this point in great detail. It is therefore the intention of this brief report to present recent uses of iodine(III) reagents like **1** or reagents derived from it in reactions with complex multifunctional substrates and in natural product synthesis.

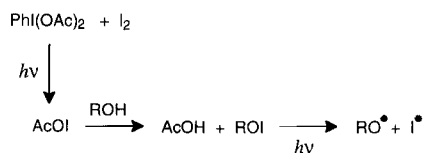
**1 1,2-Additions to Olefines**

DIB (**1**) can be used to promote 1,2-addition reactions to olefines. However, **1** is only able to transfer acetoxy groups to highly nucleophilic alkenes and cyclopentadiene [4]; isolated double bonds are inactive under mild conditions. Over the last years various procedures have been developed, where **1** is used to activate other heteroatom containing reagents, which then add to olefinic double bonds (Scheme 3). Triisopropylsilyl enol ethers are ideally suited for bisazidation under radical conditions (equ. 1) [5]. The authors propose that iodine(III) intermediate **4** adds to 2,2,6,6-Tetramethylpiperidin-1-oxyl (“TEMPO”) to give an I(IV) species which is able to generate azide radicals.  $\alpha$ -Acetoxy iodides have been prepared from indene by utilizing novel iodate(I) salts like **5** (see also Scheme 1; analogous to **2e**) [6]. These are

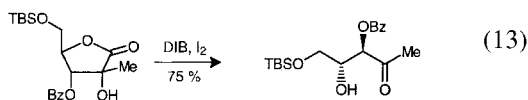
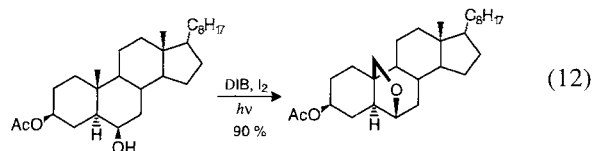


Scheme 3





Scheme 7



Scheme 8

## 6 Miscellaneous

This short report can only cover some aspects of the rich chemistry of (diacetoxyiodo)benzene (**1**). Many other applications are known of which the following are particularly worth mentioning, as they have also found use in reactions with multifunctional substrates. In the presence of **1** and in particular [bis(trifluoroacetoxy)iodo]benzene (**2a**) primary carboxamides, including peptide amides undergo facile Hofmann-type rearrangement affording amines in high yield [20]. **2a** has proven to be a very mild and efficient reagent for the dethioacetalization of dithiaacetals thereby generating the corresponding aldehydes [21]. Finally, iodine(III) reagents derived from **2b** have been used as promoters in glycosidation reactions with thioglycosides [22].

From these few examples presented here, it is obvious that DIB (**1**) promotes a rich and diverse chemistry. As the number of reagents that derive from **1** further increase, the importance of hypervalent iodine in preparative organic chemistry will further enhance.

## References

- [1] C. Willgerodt, *J. prakt. Chem.* **43** (1886) 154
- [2] Reviews: a) R. M. Moriarty, R. K. Vaid, G. F. Koser, *Synlett* **1990**, 365; b) A. Varvoglis, *The Organic Chemistry of Polycordinated Iodine*, Verlag Chemie, New York, Weinheim, Cambridge, (1992); c) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **96** (1996) 1123
- [3] J. G. Sharefkin, H. Saltzman, *Org. Synth.*, Coll. Vol. **5** (1973) 660. **1** is commercially available from Merck (Darmstadt), Fluka, Aldrich, and Lancaster; further-

more, **2a** and **2c** can also be obtained from Aldrich and Fluka

- [4] R. Criegee, H. Beucker, *Justus Liebigs Ann. Chem.* **541** (1939) 218
- [5] a) R. Moriarty, J. S. Khosrowshahi, *Tetrahedron Lett.* **27** (1986) 2809; b) P. Magnus, M. B. Roe, C. Hulme, *J. Chem. Soc., Chem. Commun.* **1995**, 263
- [6] A. Kirschning, C. Plumeier, L. Rose, *Chem. Commun.* **1997**, in press
- [7] a) M. Tingoli, M. Tiecco, D. Chianelli, R. Balducci, A. Temperini, *J. Org. Chem.* **56** (1991) 6809; b) F. Santoyo-González, F. G. Calvo-Flores, P. García-Mendoza, F. Hernández-Mateo, J. Isac-García, R. Robles-Díaz, *J. Org. Chem.* **58** (1993) 6122; c) S. Czernecki, D. Randriamandimby, *Tetrahedron Lett.* **34** (1993) 7915
- [8] S. Ray, K. Pal, C. K. Saha, *Ind. J. Chem., Sect. B* **34** (1995) 112
- [9] A. M. Turuta, A. V. Kamernitzky, T. M. Fadia, A. V. Zhullin, *Synthesis* **1985**, 1129
- [10] I. P. Andrews, N. J. Lewis, A. McKillop, A. S. Wells, *Heterocycles* **38** (1994) 713
- [11] J. Harders, A. Garming, A. Jung, V. Kaiser, H. Monenschein, M. Ries, L. Rose, K.-U. Schöning, T. Weber, A. Kirschning, *Liebigs Ann./Recueil* **1997**, 2125
- [12] a) P. Magnus, J. Lacour, *J. Am. Chem. Soc.* **114** (1992), 767; b) P. Magnus, J. Lacour, P. A. Evans, M. B. Roe, C. Hulme, *J. Am. Chem. Soc.* **118** (1996) 3406
- [13] A. Kirschning, S. Domann, G. Dräger, L. Rose, *Synlett* **1995**, 767
- [14] A. Kirschning, *J. Org. Chem.* **60** (1995) 1228
- [15] C. B. Saitz, J. A. Valderrama, R. Tapia, F. Farina, M. C. Paredes, *Synth. Commun.* **22** (1992) 955
- [16] C. Szantay, G. Blasko, M. Barczai-Beke, P. Pechy, G. Dörnyei, *Tetrahedron Lett.* **21** (1980) 3509
- [17] P. de Armas, J. I. Concepción, C. G. Francisco, R. Hernández, J. A. Salazar, E. Suárez, *J. Chem. Soc., Perkin Trans I* **1989**, 405
- [18] a) P. de Armas, C. G. Francisco, E. Suárez, *Angew. Chem.* **104** (1992) 746; b) C. G. Francisco, R. Freire, M. S. Rodriguez, E. Suárez, *Tetrahedron Lett.* **36** (1995) 2141; c) C. G. Francisco, C. C. Gonzalez, E. Suárez, *Tetrahedron Lett.* **37** (1996) 1687
- [19] C. M. Hayward, M. J. Fisher, D. Yohannes, S. J. Danishefsky, *Tetrahedron Lett.* **34** (1993) 3989
- [20] a) R. M. Moriarty, C. J. Chany, II, R. K. Vaid, O. Prakash, S. M. Tuladhar, *J. Org. Chem.* **58** (1993) 2478; b) G. M. Loudon, A. S. Radhakrishna, M. R. Almond, J. K. Blodgett, R. H. Boutin, *J. Org. Chem.* **49** (1984) 4272
- [21] G. Stork, K. Zhao, *Tetrahedron Lett.* **30** (1989) 287.
- [22] K. Fukase, A. Hasuoka, I. Kinoshita, S. Kusumoto, *Tetrahedron Lett.* **33** (1992) 7165

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