

SYNLETT Spotlight 344

Iodobenzene Diacetate – Efficient Terminal Oxidant for Transition-Metal-Mediated Transformations



Compiled by Ioana Dumitru

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

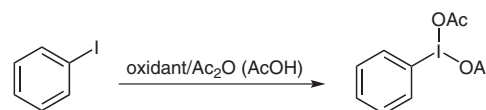
Ioana Dumitru was born in Bucharest, Romania in 1981. She received a B.Sc. in Chemistry in 2005 and her M.Sc. in 2007 from the University of Bucharest. Presently she is working towards her Ph.D. under the supervision of Prof. Dr. Ion Baciú in collaboration with Dr. Daniel Funeriu, Marie Curie Excellence Team, at the University of Bucharest. She was a recipient of a doctoral scholarship from DAAD in 2007–2008. Her current research is focused on the one-pot preparation of fused quinoxalines and the development of new methods for the synthesis of new polymeric bioconjugates.

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Introduction

The most important use of hypervalent iodine compounds is as oxidizing agents replacing many other toxic reagents, usually based on heavy metals. Also, it has been observed that the synthetic properties of trivalent iodine compounds are often similar to those of lead and thallium derivatives, somehow with better yields and improved toxicity. The iodobenzene diacetate (most used acronyms are DIB or PIDA), a trivalent iodine derivative, which presents itself as white crystalline powder, is a prominent member. It has found multiple applications in organic chemistry as efficient and inexpensive reagent.¹ Recently, its ability to act

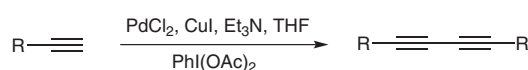
as terminal oxidant in palladium-, gold- or copper-mediated transformations was disclosed and subsequently demonstrated. DIB is commercially available and can also be easily prepared by oxidation of iodobenzene with hydrogen peroxide urea complex in the presence of acetic anhydride,^{2a} peracetic acid,^{2b} or sodium perborate^{1a} (Scheme 1).



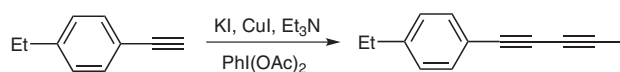
Scheme 1

Abstracts

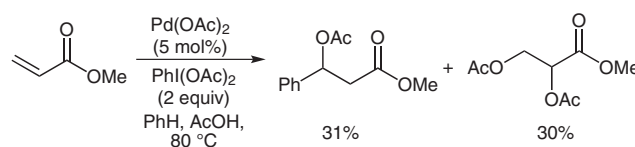
(A) The dimerization of terminal acetylenes can be achieved using DIB as oxidant under palladium- or copper-catalyzed conditions. Thereby, diynes can be prepared (with almost quantitative yields) rapidly and at room temperature.³



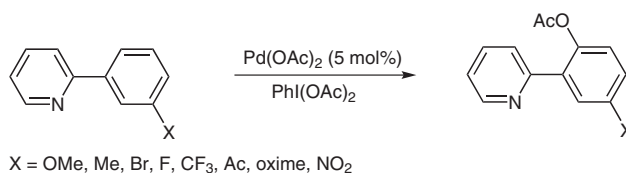
(B) Yan et al. reported a new method for the synthesis of 1-iodoalkynes by the reaction of a series of terminal alkynes with DIB, KI, and Et₃N in the presence of a catalytic amount of CuI at room temperature. The products were obtained in good to excellent yields under mild conditions in 30 minutes.⁴



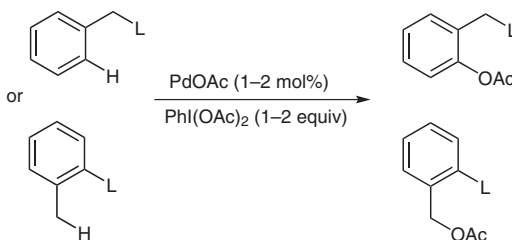
(C) A palladium-catalyzed three-component coupling reaction, which is of interest because of the potential for reduction in the number of synthetic steps, was developed by Moran and co-worker. The methacrylates were converted into aldol-type products by PhI(OAc)₂.⁵



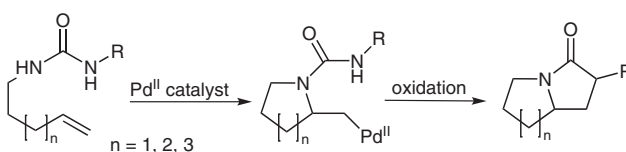
(D) Likewise, DIB can be used for the acetoxylation of *meta*-substituted arene substrates. This reaction presents remarkably functional group tolerance with respect to the *meta* substituent on the arene, and exhibits high levels of regioselectivity for functionalization at the less sterically hindered *ortho* position.⁶



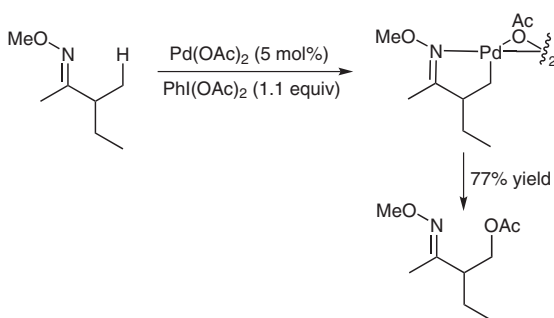
(E) Dick and colleagues reported a Pd(OAc)₂-catalyzed method for the selective acetoxylation of arene and alkane C–H bonds using PhI(OAc)₂ as a stoichiometric oxidant. These transformations proceeded under mild conditions (≤100 °C) and with very high (generally >99%) regioselectivity with substrates containing coordinating functional groups (L). L groups serve to bind to the palladium catalyst and direct C–H activation and subsequent oxidation to a specific C–H bond within the molecule.⁷



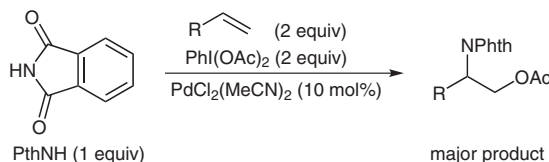
(F) With Pd(OAc)₂ as precatalyst and PhI(OAc)₂, diamination and concomitant formation of five-, six- or seven-membered fused rings were conveniently accomplished. All reactions reach high to full conversion despite of metal deactivation by the diamine products.⁸



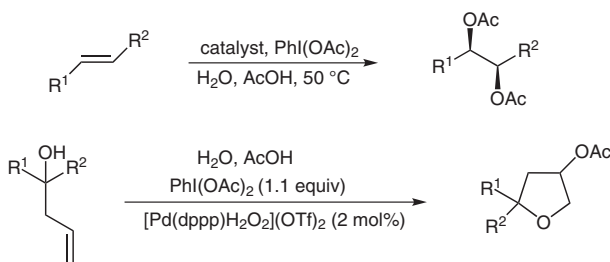
(G) Unactivated sp³ C–H bonds of oxime and pyridine substrates undergo highly regio- and chemoselective palladium(II)-catalyzed oxygenation using PhI(OAc)₂ as a stoichiometric oxidant. The C–H activation to form a palladacyclic intermediate and the oxidative cleavage [via oxidation to Pd(IV) followed by C–O bond forming reductive elimination] unfolds with high levels of stereoselectivity.⁹



(H) Stahl and Liu reported the first examples of intermolecular palladium-catalyzed aminoacetoxylation of terminal alkenes using PhI(OAc)₂ as an oxidant.¹⁰



(I) Both inter- and intramolecular olefin dioxygenation can be achieved using DIB and a palladium cationic complex. The method represents a promising compliment to the Sharpless dihydroxylation. This strategy is not limited to terminal olefins or alkenes bearing a directing group.^{11a,b}



References

- (1) (a) Zhdankin, V. V. *Arkivoc* **2009**, (i), 1. (b) Zhdankin, V. V.; Stang, P. J. *Chem Rev.* **2008**, *108*, 5299; and references cited therein.
- (2) (a) Sharefkin, J. G.; Saltzman, H. *Org. Synth., Coll. Vol. V* **1973**, 660. (b) Page, T. K.; Wirth, T. *Synthesis* **2006**, 3153.
- (3) Yan, J.; Lin, F.; Yang, Z. *Synthesis* **2007**, 1301.
- (4) Yan, J.; Li, J.; Cheng, D. *Synlett* **2007**, 2442.
- (5) Rodriguez, A.; Moran, W. J. *Eur. J. Org. Chem.* **2009**, 1313.
- (6) Kalyani, D.; Sanford, M. S. *Org. Lett.* **2005**, *7*, 4149.
- (7) Dick, A. R.; Hull, K. H.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300.
- (8) Streuff, J.; Hovelmann, C. H.; Nieger, M.; Muiz, K. *J. Am. Chem. Soc.* **2005**, *127*, 14586.
- (9) Desai, L. V.; Hull, K. H.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9542.
- (10) Liu, G.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 7179.
- (11) (a) Li, Y.; Song, D.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2962. (b) Wang, W.; Wang, F.; Shi, M. *Organometallics* **2010**, *29*, 928.