

Direct Conversion of Secondary Phosphine Oxides and *H*-Phosphinates with [Di(acyloxy)iodo]benzenes to Phosphinic and Phosphonic Amides

Anna Hubacz and Sławomir Makowiec

Department of Organic Chemistry, Faculty of Chemistry, Gdansk University of Technology, Narutowicza 11/12; Gdańsk 80-952, Poland

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ABSTRACT: *The reaction of [di(acyloxy)iodo]benzene with secondary phosphine oxides or H-phosphinates in the presence of primary or secondary amines allows one to obtain phosphinic or phosphonic acids amides in the one-pot process. We take advantage of the strong acylating system DAIB/R₂P(O)H to phosphinylation of amines. However, the reaction mechanism is multipathway and causes yields of phosphinic or phosphonic acids amides to be moderate. When the concentration of amines is low, the intermolecular process plays a main role leading to the formation of carboxylic amides through mixed phosphoric–carboxylic anhydride, and also in the low concentration of amines, tetrahydrofuran effectively competes with the amines in the nucleophilic attack on the acylating intermediates.* © 2009 Wiley Periodicals, Inc. *Heteroatom Chem* 20:81–86, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20514

INTRODUCTION

Despite the fact that first hypervalent organoiodine compound was synthesized by Wilgerodt in 1886 [1], and hypervalent iodine reagents are widely

used in organic transformations [2,3], reactivity of hypervalent organoiodine compound with organophosphorus reagents is still considerably unexplored area. There are only a few publications concerning reactions of usual hypervalent organoiodine reagents as [di(acetoxy)iodo]benzene, [bis(trifluoroacetoxy)iodo]benzene, iodozobenzene, or dichloroiodobenzene with phosphorus nucleophiles. In 1978, Foss published work concerning oxidation of diphosphines and trialkyl phosphites with iodozobenzene [4]. Lopusinski carried out a set of experiments between phosphorus organic reagents such as triphenylphosphine, trialkyl phosphites, triarylphosphites with iodozobenzene and iodoxybenzene in the presence of montmorillonite or in the absence of such a catalyst [5]. Garreg et al. tried to use [di(acetoxy)iodo]benzene as a mild reagent for oxidation of *H*-phosphonates to phosphates in oligonucleotide synthesis [6]. An interesting aspect of the reactivity of hypervalent iodine organic compounds with phosphorus nucleophiles is the direct arylation of phosphorus acid salts [7], trialkyl phosphites [8], or phosphines [9] using arylidonium salts.

Phosphorus analogs of Koser reagent [hydroxy((phosphoryl)oxy)iodo]benzenes and their reactivity exemplify an interesting aspect of hypervalent iodine and phosphorus organic chemistry, particularly α -phosphoryloxylation of ketones [10,11] and preparation of alkynyl dialkyl phosphates [12].

Correspondence to: Sławomir Makowiec; e-mail: mak@chem.pg.gda.pl.
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