

# Reactivity of Diacyloxyiodobenzenes Toward Trivalent Phosphorus Nucleophiles

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**ABSTRACT:** *The reaction of diacyloxyiodobenzenes and tetravalent phosphorus nucleophiles was investigated. It was established that both H-phosphonates and secondary phosphine oxides react with diacetoxyiodobenzene in alcohols in the presence of sodium alcoholates yielding trialkyl phosphates and alkyl phosphinates respectively. For this transformation reactive intermediate **6** is proposed. In contrast to this, the treatment of diacetoxyiodobenzene with 3 equiv of sodium diisopropyl phosphite in THF produces diisopropyl 1-(diisopropoxyphosphinyl)ethylphosphonate with excellent yield. It was found that diacyloxyiodobenzene/PR<sub>3</sub> system may serve as an acylating agent; the acylation process can proceed via carboxylic acid anhydride or acylphosphonium salt **17** depending on the protocol used. New very efficient method for synthesis of 2,4,6-trimethylbenzoic anhydride was developed. © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:352–359, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10161*

## INTRODUCTION

[Bis(acyloxy)iodo]arenes are the most important, well investigated, and useful organic derivatives of iodine(III). Two of these, diacetoxyiodobenzene and [bis(trifluoroacetoxy)iodo]benzene, are commercially available or can be easily prepared by ox-

dation of iodobenzene with the respective peracid. In the last 20 years [bis(acyloxy)iodo]arenes have found widespread application as general, universal oxidizing reagents, and radical initiators [1]. Primary carboxamides undergo readily a Hofmann-type rearrangement with several iodanes, leading to amines or some of their derivatives. The reagent of choice for this rearrangement appears to be PhI(OOCCH<sub>3</sub>)<sub>2</sub>, as well as PhI(OOCCF<sub>3</sub>)<sub>2</sub>, both of which are used with a large variety of amides [2].

To the best of our knowledge polyvalent iodine compounds have not been explored extensively in the field of organophosphorus chemistry. As early as 1977, Foss et al. [3] presented the effectiveness of iodosylbenzene in the oxidation of the trivalent phosphorus organic compounds phosphines and diphosphines, which were transformed into phosphine oxides. For this transformation a phosphorus attack on the oxygen atom of iodosylbenzene was suggested. In 1979, the synthesis of [hydroxy-[(bis(phenyloxy)phosphoryl)oxy]iodobenzene in the reaction of diacetoxyiodobenzene with diphenyl phosphate in aqueous acetonitrile was published [4]. This compound generally has a reactivity pattern similar to [hydroxy(tosyloxy)iodo]benzene. It reacts with enolizable ketones affording the products of  $\alpha$ -phosphoryloxylation [5].

Recently we investigated the reaction of iodosylbenzene with  $>P(O)H$  acids, which in aprotic solvents yields oxidation products, i.e.  $>P(O)OH$  acids and/or  $>P(O)OP(O)<$  anhydrides. If the reaction is performed in alcohol ROH as solvent in the presence of sodium alcoholate, a  $>P(O)OR$  ester is the major product [6].

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