SYNLETT
Spotlight 232

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

(Dichloroiodo)benzene ($PhICl_2$)

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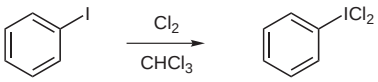
Introduction

(Dichloroiodo)benzene ($PhICl_2$) was first prepared in 1886; its chemistry then became an intensely studied topic because of its wide application as an effective chlorinating or oxidizing agent in various organic reactions.[1] As a chlorinating agent, (dichloroiodo)benzene can be applied not only to the addition of chlorine to alkenes, but also to the chlorination with other substrates, such as alkanes, ethers, esters, thioethers, ketones, sulfoxides, steroids, etc., with moderate to high yields.[1,2] (Dichloroiodo)benzene can oxidize aldoximes and ketoximes to nitrile oxides[3] and ketones,[4] respectively in good yields. In this spotlight, recent applications using $PhICl_2$ in organic syntheses are summarized.

Preparation

(Dichloroiodo)benzene was prepared by bubbling chlorine gas through a solution of iodobenzene in chlorinated solvents,[5] which had been applied to an industrial-scale preparation (Scheme 1).[6]



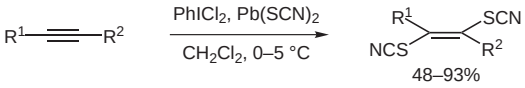
Scheme 1

Properties

(Dichloroiodo)benzene exists as yellow crystalline solid with mp 110–112 °C. It is not stable on long standing, which means that it is normally prepared and used fresh for subsequent applications.

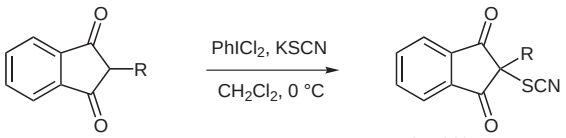
Abstracts

(A) Alkynes can be effectively thiocyanated by the combination of $PhICl_2/Pb(SCN)_2$ in dichloromethane to yield the corresponding alkenes with high *E*/*Z* ratio.[7]

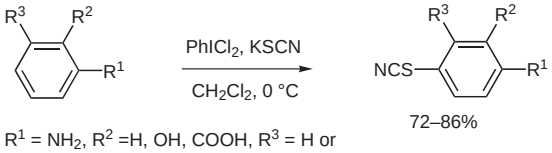


R^1 = Ph, *p*-MeC_6H_4, *n*-Pr, $Me(CH_2)_n$, (n = 3, 5, 7) $HO(CH_2)_4$, 1-cyclohexenyl; R^2 = H, Me, Ph, TMS

(B) A combination of $PhICl_2$/KSCN can thiocyanate β-dicarbonyl compounds, phenols as well as anilines to the corresponding thiocyanato derivatives in dichloromethane.[8]



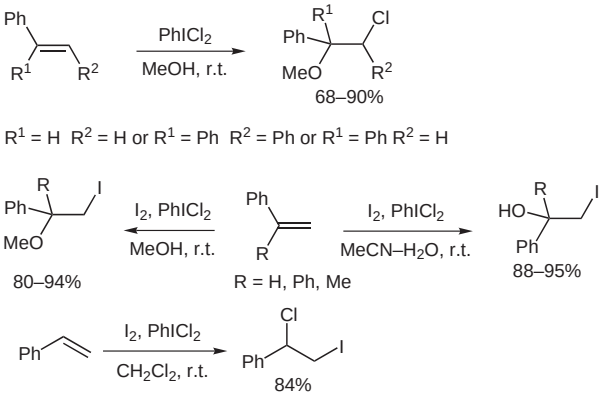
R = Ph, *p*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$



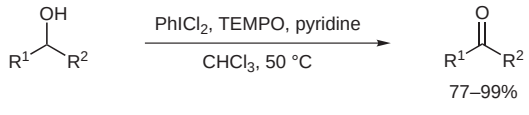
R^1 = NH_2, R^2 =H, OH, COOH, R^3 = H or R^1 = OH, R^2 = H, OH, R^3 = H

SYNLETT 2008, No. 5, pp 0782–0783
Advanced online publication: 26.02.2008
DOI: 10.1055/s-2008-1032173; Art ID: V23707ST

(C) $PhICl_2$ can be used for the chloromethoxylation, iodomethoxylation, iodohydroxylation, and iodochlorination of alkenes under different conditions with good yields.[9,10]

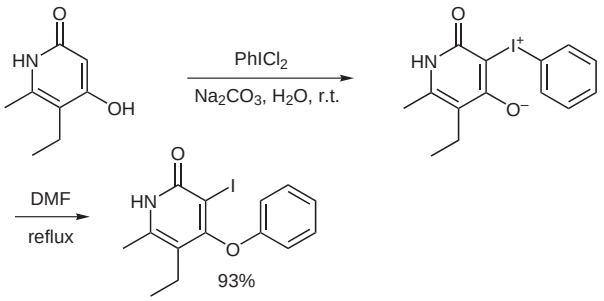


(D) Aliphatic primary and secondary alcohols can be oxidized to the corresponding aldehydes and ketones in good to excellent yields by the combination of $PhICl_2$/2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO)/pyridine in $CHCl_3$. This oxidizing system has preference to oxidize secondary alcohols over primary ones.[11]

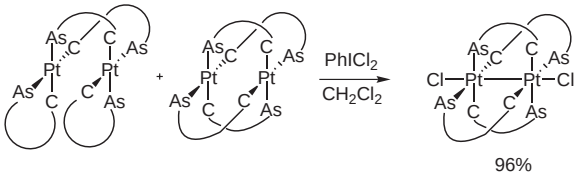


R^1 = 4-(2-tetrahydropyranyloxy)-2-butenyl, 2-isopropyl-5-methylcyclohexyl, $Me(CH_2)_7$, $Me(CH_2)_9$, $Me(CH_2)_{15}$, benzyl; R^2 = H or R^1 = $Me(CH_2)_6$, Ph; R^2 = Me

(E) Reactions of $PhICl_2$ with 4-hydroxypyridin-2-ones in aq Na_2CO_3 gave an aryliodonium ylide that rearranged to 3-iodo-4-phenoxypyridinones. This operation can install both the iodine and aryloxy groups to the pyridinone nucleus.[12]



(F) $PhICl_2$ is a good reagent for the oxidative chlorination of various metal complexes.[13] For example, treatment of dinuclear platinum(II) complexes as a mixture of isomers (the half-lantern and lantern complexes) with $PhICl_2$ in dichloromethane gave the dichlorodiplatinum(III) lantern complex in excellent yield.[14]



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