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Iodine Monochloride
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Introduction

Iodine monochloride is a chemical compound with the formula $\text{ICl}$. Because of the difference in the electronegativity of iodine and chlorine, ICl is highly polar and behaves as a source of $\text{I}^+$. Iodine monochloride is a low melting black or brownish-red solid and widely available (usually in 97–98% purity). It is soluble in alcohol, ether, CS$_2$, acetic acid, acetone and pyridine and hydrolyzes in water to HCl and IOH. ICl explodes on contact with potassium metal, mixes with sodium metal, and it can explode if impacted. Its reaction with PCl$_3$ is extremely exothermic.\(^1\) Iodine monochloride can be easily prepared by adding an aqueous solution of potassium iodate to potassium iodate dissolved in concentrated HCl, in a closed vessel to avoid the loss of chlorine.\(^2\) Iodine monochloride is a versatile reagent for the synthesis of a large number of organic compounds being employed, for example, as a source of electrophilic iodine in the synthesis of certain aromatic iodides.\(^3\) It cleaves C–Si bonds\(^4\) and can be used in the electrophilic addition to the double bond in alkenes leading to chloroiodoalkanes.\(^5\) When iodine monochloride is reacted with sodium azide in situ, the iodoazide product is obtained.\(^6\) Other examples of synthetic applications of this reagent also include electrophilic substitutions in Csp\(^2\) and electrophilic cyclizations.\(^7\)–\(^9\)

Abstracts

(A) Do and Daugulis showed that the iodination of pentachlorobenzene using a combination of iodine chloride and t-BuOLi in DMF occurs in excellent yield (90%). Fluorine aromatic compounds like 1,3,5-trifluorobenzene can be either mono- or triiodinated in acceptable yields, depending on the ratio of the halobenzene to the iodine chloride.\(^3\)

(B) Silylthiophene derivatives as 3,4-difluoro-2,5-bis(trimethylsilyl)thiophene can be submitted to an electrophilic substitution reaction with iodine chloride in anhydrous carbon tetrachloride to give 3,4-difluoro-2,5-diodothiophene in 80% yield.\(^4\)
(C) The addition of ICl to (Z)- and (E)-2-butene occurs in an anti-stereospecific manner: the erythro-2-chloro-3-iodobutane can be formed by the addition of ICl to (E)-1-butene, while the other isomer (threo) is formed by the addition of ICl to (Z)-1-butene.5

(D) In their research efforts to modify citidine nucleosides, Verheyden and Moffatt showed that the treatment of enol ether nucleoside 1 with iodine azide, generated in situ from iodine chloride and sodium azide, afforded the 4′-azido nucleoside derivative 1a.6

(E) Goodman et al. reported the reaction between 2[β-carbo(2-fluoroethoxy)-3-{3′-[Z]-2-trimethylstannylethenyl]phenyl]nortropane (2) and ICl, leading to compound 4 in good yield. Similar results were obtained in the case of 2[β-carbo(2-fluoropropoxy)-3β-[3′-[Z]-2-trimethylstannylethenyl]phenyl]nortropane (3).7

(F) A set of 4-iodoisocoumarins were efficiently prepared by electrophilic cyclization of ortho-(1-alkynyl)benzoates using iodine monochloride in dichloromethane.8

(G) Electrophilic cyclization of 2-chalcogene alkynyl anisole using ICl as an electrophile source produced 3-iodo-2-(phenylselenyl)benzofuran in good yield. Manarim et al. reported that for this type of reaction the product distributions were strongly dependent on the nature of the substituents in the aromatic ring of anisole and on the chalcogen atom directly bonded to the triple bond.9

References