

Iodine in organic synthesis

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Commercially available iodine has played an important role in organic synthesis. This review discusses the versatile uses of iodine in different chemical transformations. Reactions include esterification, cycloaddition reaction, allylation of aldehydes, acetalization of carbonyl compounds, acylation of alcohols, synthesis of cyclic ethers and aromatization of α,β -unsaturated ketones.

Keywords: Cycloaddition, Esterification, Iodine, Organic synthesis

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Introduction

Selective functional group transformation of complex molecules to target compounds is the most important requirements of modern organic synthesis. The lack of selectivity blocks the road for obtaining the desired compounds. Iodine, commercially available brown solid, m p 113°C, has found widespread use not only in conduction of selective transformation but also shown interesting and varied reactions. The present review concentrates on the utility of iodine in certain organic transformations, excluding iodolactonization and iodocyclization studies¹⁻⁵.

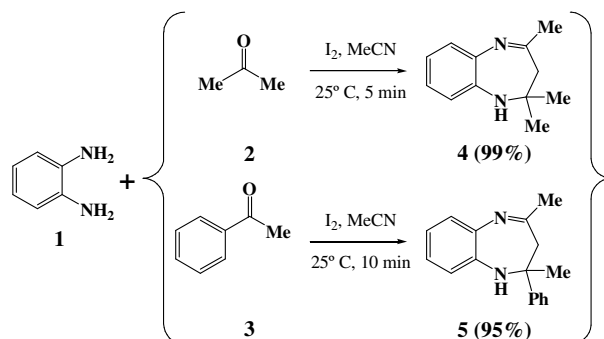
Synthesis of Benzodiazepine Derivatives

Synthesis of 1,5-benzodiazepine derivatives from phenyldiamines and acyclic ketones under mild conditions in presence of iodine as catalyst has been reported⁶. O-Phenyldiamine **1** with acyclic ketone **2** and cyclic ketone **3** yields benzodiazepines **4** and **5** respectively (Scheme I). Such synthesis can also be accomplished in presence of other catalysts (boron trifluoride etherate, sodium borohydride, polyphosphoric acid, silicon dioxide, etc.) but these procedures suffer from drastic reaction conditions, low to moderate yield and occurrence of several side reactions. Iodine helps to carry out reactions under neutral and mild condition and in high yield. In addition, work-up procedure is very simple and reaction can be performed at room temperature.

Esterification and Transesterification

Iodine has been utilized as Lewis acid catalyst for esterification⁷ of acids (saturated, unsaturated, hydroxy and dicarboxylic acids) with alcohols. Thus, conversion of acids **6-7** to corresponding esters **8-9** has been accomplished in high yield by heating with methanol at refluxing temperature (Scheme II). Esters of tertiary alcohols, which are difficult to prepare, can be obtained by heating the acid with t-butanol but it requires longer reaction period and increased amount of catalyst. The carboxylic acid group, directly attached to aromatic ring such as benzoic acid, p-nitrobenzoic acid, can not be esterified.

Transesterification of esters with alcohols have been accomplished using molecular iodine. Thus esters **10-11** on heating with alcohols (n-butanol) in presence of iodine are converted to esters **12-13**

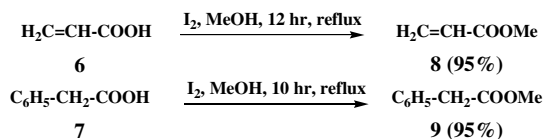


Scheme I

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Scheme II

respectively (Scheme III). Vegetable oils (castor, peanut, coconut, jatropha) have been smoothly transesterified with methanol. Esterification and transesterification reactions are highly sensitive to moisture but the reaction catalyzed by iodine does not require special precaution to exclude moisture or air from the system. Simultaneous esterification and transesterification reactions can also be accomplished using iodine.

Allylation of Aldehydes

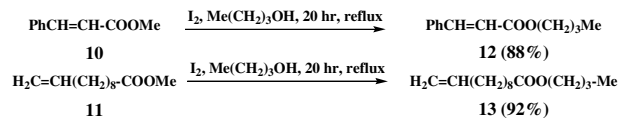
Several aldehydes (aromatic and aliphatic) can be converted to the corresponding homoallylic alcohols with allylic trimethylsilane in presence of iodine in acetonitrile⁸. Thus the homoallylic alcohols **16-17** have been obtained in high yield from the corresponding aldehydes **14-15** (Scheme IV). These reactions proceed smoothly at 0°C and with high selectivity. The resulting products can be isolated after a short reaction period.

Cycloaddition Reactions

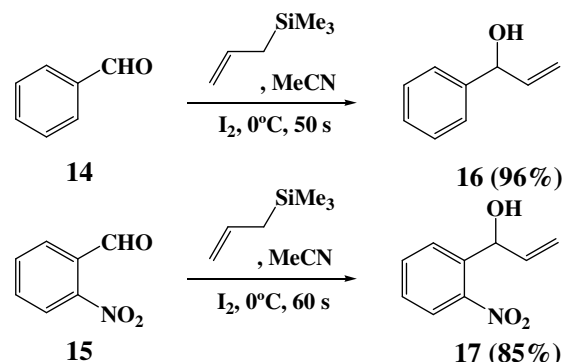
Intramolecular (4+2) cycloaddition⁹ of O-quinonemethanes (generated *in situ* from O-hydroxybenzaldehydes) and unsaturated alcohol has been accomplished in presence of trimethyl orthoformate (TMOF) and elemental iodine to obtain the corresponding *trans*-annulated pyrone 3,2-c benzopyrans in high yields with high diastereoselectivity (Scheme V). This method has provided a useful method for the synthesis of benzopyrans **21-22** respectively from hydroxybenzaldehydes **18-19** and unsaturated alcohol **20**. The remarkable advantages that have been noted in use of elemental iodine in this cycloaddition include high yield, mild reaction condition, high diastereoselectivity, short time period and simplicity in operation.

Hydrides from Alcohol

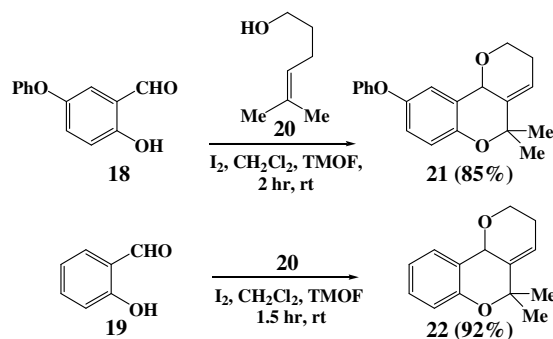
A variety of substituted benzohydrols **23-24** have been reduced by a mixture of hypophosphorous acid (H₃PO₂) and iodine in acetic acid to the corresponding methylene derivatives **25-26** in high yield¹⁰ (Scheme VI). Acetic acid is the best solvent for these transformations. The present method would be prefer-



Scheme III



Scheme IV

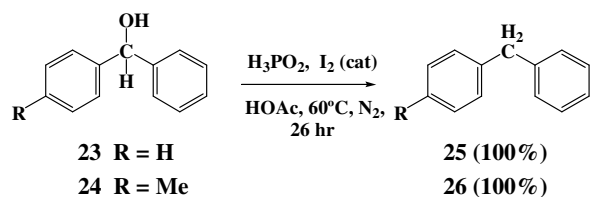


Scheme V

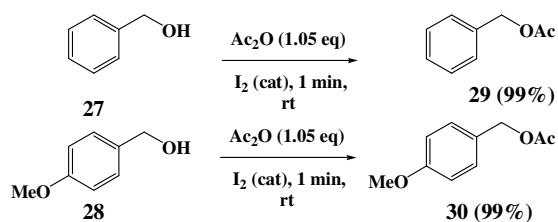
red not only in terms of cost and yield but easy manipulation in comparison with previous methods¹⁰ for deoxygenation of benzohydrols.

Acylation of Alcohols

Acetyl group is widely applied in protection of the hydroxyl functionality in organic synthesis¹¹. An excellent method for acylation of alcohols (primary, secondary, tertiary) and benzylic alcohols with acetic anhydride has been developed¹² under solvent-free conditions in presence of iodine at room temperature. The conversion of many alcohols **27-28** to respective **29-30** acetates has been accomplished in high yield utilizing this procedure (Scheme VII). The reaction is very slow in absence of iodine and the functional groups like chloro, double and triple bonds are not affected during the reaction. It is necessary to indicate



Scheme VI



Scheme VII

that there exists many catalysts¹², which can be utilized for acetylation, but they suffer from many disadvantages and therefore iodine appears the most convenient and efficient catalyst for acetylation.

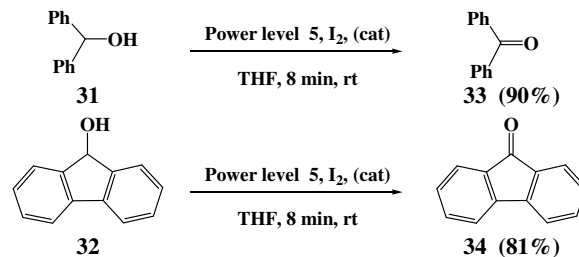
Oxidation of Benzylic Alcohols

Many methods have been developed for the oxidation of alcohols to aldehydes and to ketones because this is a common reaction in organic synthesis¹³. Recently, Banik *et al*¹⁴ have shown (Scheme VIII) that iodine can be used in the oxidation of benzylic alcohols **31-32** to the corresponding ketones **33-34** respectively in high yield, under microwave irradiated method.

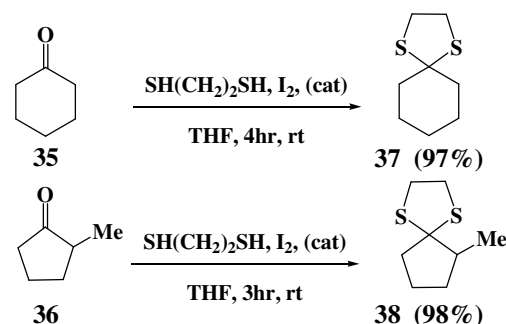
Protection of Carbonyl and Hydroxyl Groups

Protection of carbonyl group and hydroxyl group becomes necessary requirement during the synthesis of multifunctional organic molecules. Blocking of carbonyl group as thioketals is widely used owing to its stability toward a wide range of reagents. Thioketalization is usually performed in presence of acids¹⁵. Recently, the thioketalization of several aldehydes and ketones has been carried out in tetrahydrofuran in presence of catalytic amount of iodine¹⁶. Probably hydroiodic acid is the actual catalyst involved in this reaction. This method can be applied in transformation of carbonyl compounds **35-36** to corresponding thioketals **37-38** respectively (Scheme IX).

The present method can also be applied for the selective protection of ketone in presence of another in a complex molecule. Iodine has proven useful in



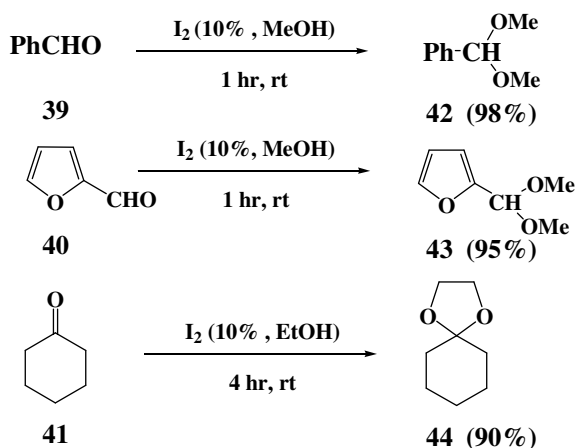
Scheme VIII



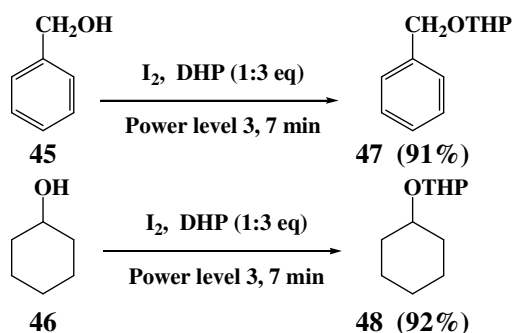
Scheme IX

chemoselective¹⁷ thioacetalization of carbonyl functions and trans thioacetalization of O, O and S, O-acetals and acylals. Dithioacetalization of aldehydes and ketones has been performed in high yield in presence of catalytic amount of iodine supported on alumina surface¹⁸. The reaction can be carried out under mild, neutral and solvent free conditions. The conversion of carbonyl group to dithioacetal or dithioketal has been reported employing samarium and iodine in acetonitrile¹⁹. Not only thioketal, carbonyl group has also been protected as acetals and ketals. The reaction is generally performed in presence of acids but this process suffers from several defects namely long reaction time, reflux temperature, undesired side reactions and non-selectivity. These difficulties have been overcome by using iodine²⁰. Thus aldehydes **39-40** and ketone **41** have been protected as acetals **42-43** and ketal **44** respectively by using catalytic amounts of iodine and methanol or ethanol (Scheme X).

Iodine catalyzed acetalization is simple, mild, selective and new. The utility of iodine has been in the conversion of several types of carbonyl compounds to their 1,3-dioxanes by the use of 1,3-bis(trimethylsiloxy) propane (BTSP) and a catalytic amount iodine has recently been reported²¹. It is known that protection of hydroxyl group as tetrahy-



Scheme X



Scheme XI

dropranyl ether is very common in schemes of an organic synthesis strategy. Protection of hydroxyl group as tetrahydropyranyl ether has been accomplished with several reagents²². Deka & Sharma²³ have shown that protection of alcohols as their tetrahydropyranyl ethers in high yield can be performed without any difficulty through a microwave irradiated reaction catalyzed by iodine. Scheme XI illustrates the conversion of alcohols **45-46** to the corresponding tetrahydropyranyl ethers **47-48** using this method. Selective protection of one hydroxyl group as its tetrahydropyranyl ether in 1, n-symmetrical diol (ethane-1,2-diol, propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, cyclohexane-1,4-diol, etc.) has been reported²⁴ by microwave irradiation of the diol with dihydropyran catalyzed by iodine.

Reduction

In reduction of various functional groups, iodine has proven to be an important reagent in organic synthesis. It has been reported²⁵ that reduction of olefinic double bond of several α, β -unsaturated carboxylate acid derivatives can be realized with metallic samarium and iodine in alcohol at room temperature to the

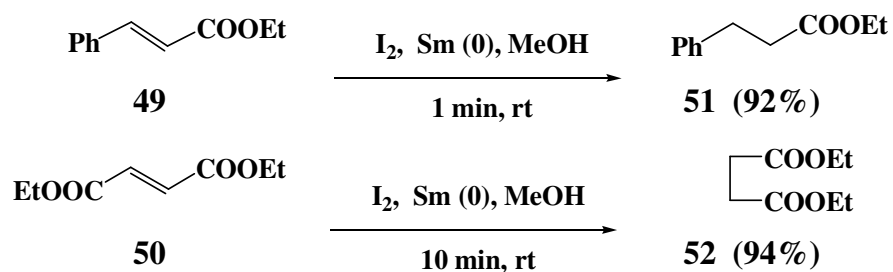
corresponding saturated products in high yield. The 1, 4-reduction is very slow in absence of iodine. It can be observed that unsaturated esters **49-50** undergo smooth conversion to the corresponding saturated esters **51-52** (Scheme XII). The reaction is rapid and carried out in protic solvent under mild condition. Chinese scientists have observed that aromatic nitro compounds can be reduced to the corresponding primary amines and hydrazines in high yield using samarium metal in presence of catalytic amount of iodine under aqueous media²⁶. Banik *et al* have also demonstrated²⁷⁻³⁰ the use of samarium metal and iodine in reduction of aromatic nitro compounds and imines to the amino derivatives. Halogen and amido substituents on aromatic ring remain unaffected during the reaction. Utility of iodine has also been demonstrated³¹ in the regioselective reduction of the α, β -double bond of some naturally occurring dienamides using sodium borohydride and iodine system.

Cyclic Ether

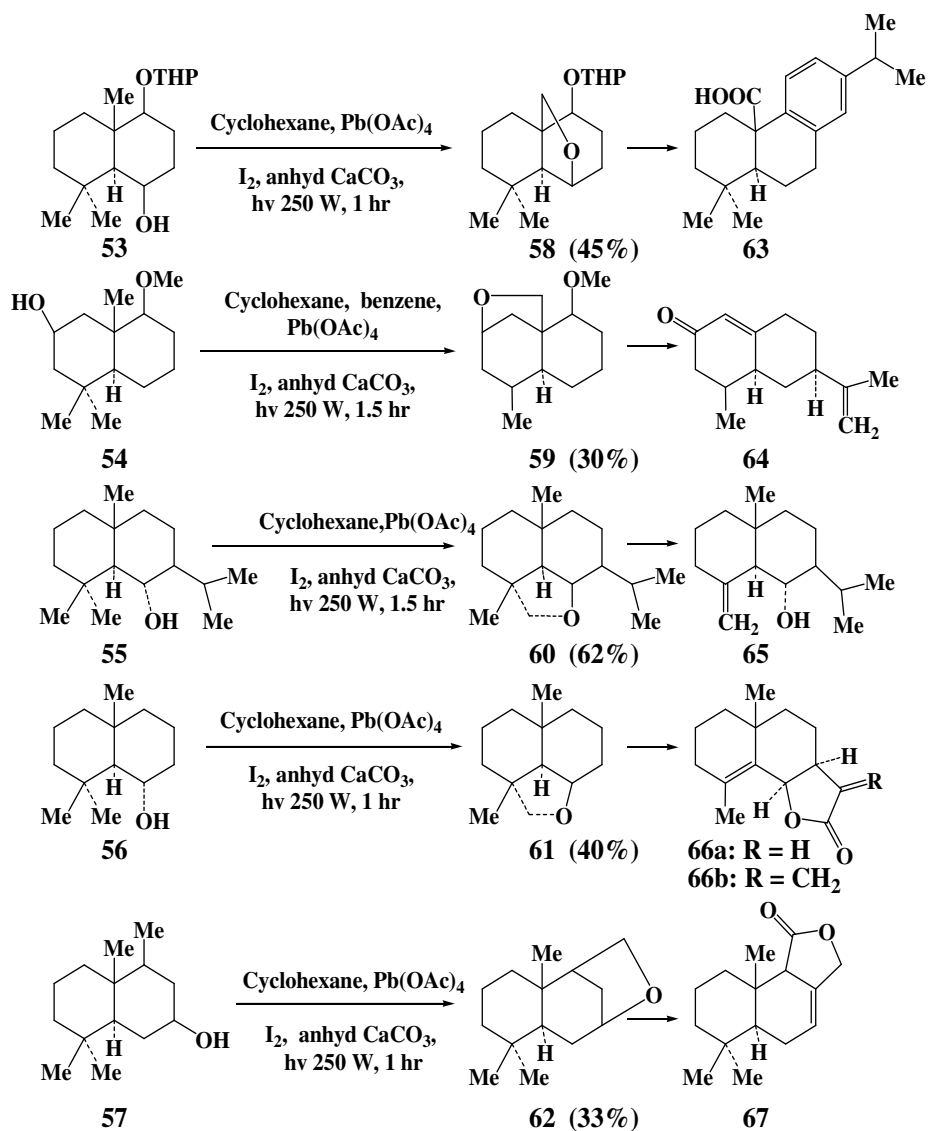
Several cyclic alcohols **53-57** (angular methyl group) have been converted³²⁻³⁶ by heating with lead tetraacetate and cyclohexane in presence of iodine to respective cyclic ethers **58-62**, which proved potential intermediates for the total synthesis of pisiferic acid **63**, glutonisonone **64**, juneno **65**, lactone **66(a)**, frullanolide **66(b)** and drimenin **67** respectively (Scheme XIII). Synthesis of several cyclic ethers and their utility in the synthesis of terpenoid compounds has been discussed in detail³⁷.

Aromatization of α, β -Unsaturated Ketones

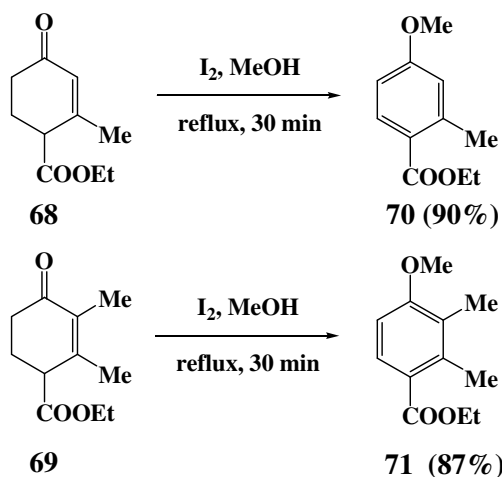
Iodine in alcohol has been utilized for the aromatization of several α, β -unsaturated ketones and esters. Kotnis has reported³⁸ aromatization of a wide variety of Hagemann's ester **68-69** to the corresponding p-methoxybenzoate derivatives **70-71** respectively (Scheme XIV). The precursor in almost all synthesis to antibiotic milbemycin β_3 is highly functionalized p-methoxybenzoate derivative. A short and efficient synthesis of p-methoxybenzoate has been developed with the aid of aromatization process of unsaturated ketones. The aromatized products can be transformed to p-methoxybenzoic acids and p-hydroxybenzoates, which is a common subunit present in many marine natural products³⁹. Study of Kotnis is based on the observation of Tamura & Yoshimoto⁴⁰ who reported aromatization of cyclo-hexenone using iodine and methanol at reflux.



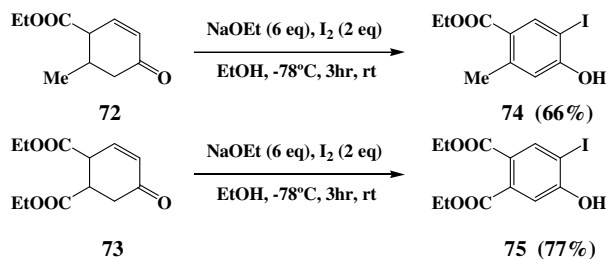
Scheme XII



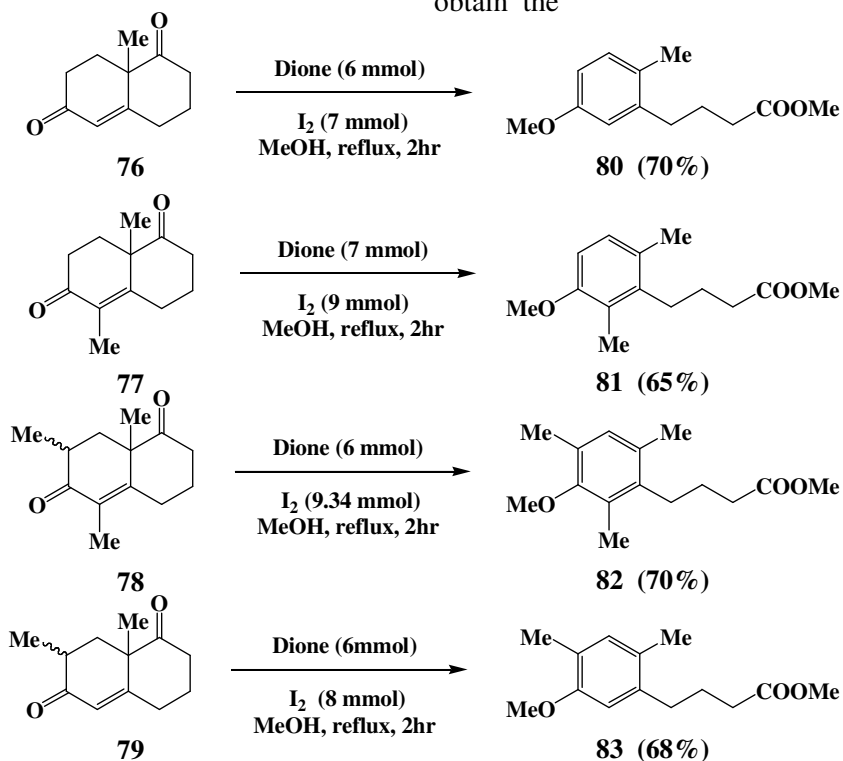
Scheme XIII



Scheme XIV



Scheme XV

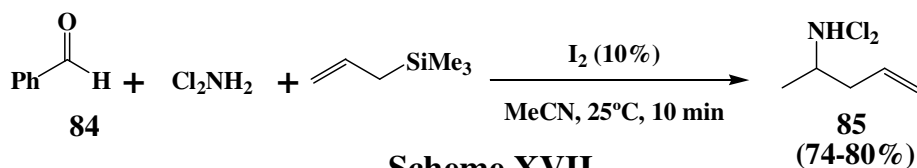


Scheme XVI

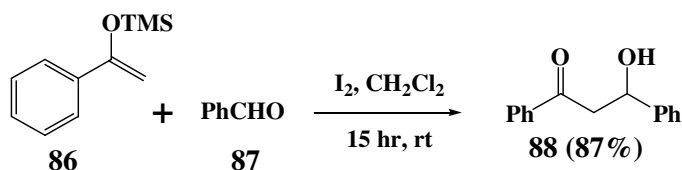
Transformation of a wide variety of easily accessible 2-cyclohexenone-4-carboxylates **72-73** to the corresponding iodophenols **74-75** in high yield has been accomplished⁴¹ with iodine and sodium ethoxide in ethanol (Scheme XV). 2-Iodophenols are versatile building blocks for synthesis of a variety of benzoheterocyclic systems. Several unsaturated cyclohexenone derivatives undergo oxidative aromatization⁴² with iodine-cerium (IV) ammonium nitrate in alcohol (methanol, ethanol, 1-propanol, 2-propanol) affording the corresponding alkyl phenyl ethers in good yield. Banerjee *et al.*⁴³ recorded aromatization and fragmentation of cyclic diones **76-79** on treatment with iodine and methanol affording anisole derivatives **80-83** respectively (Scheme XVI). These examples represent the first report of aromatization and fragmentation of cyclic diones with iodine and methanol.

Miscellaneous

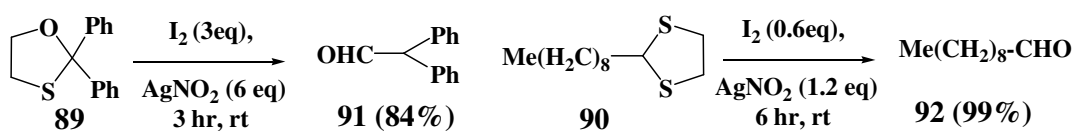
Phukan⁴⁴ observed the utility of iodine in condensation of aldehydes **84**, benzyl carbamate and allyl trimethylsilane for the synthesis of protected homoallylic amine **85** (Scheme XVII). An efficient and convenient procedure for Mukaiyama aldol reaction of silyl enolate **86** and carbonyl compound **87** has been accomplished catalyzed by iodine to obtain the



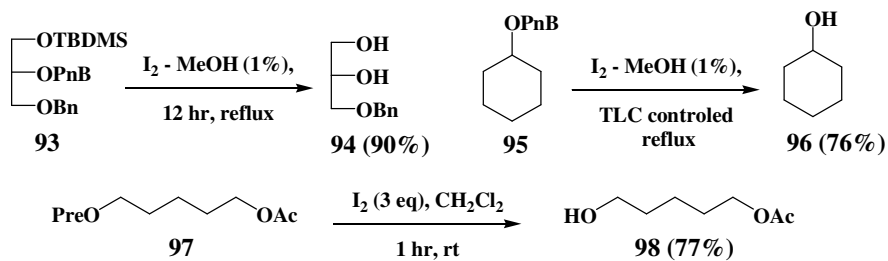
Scheme XVII



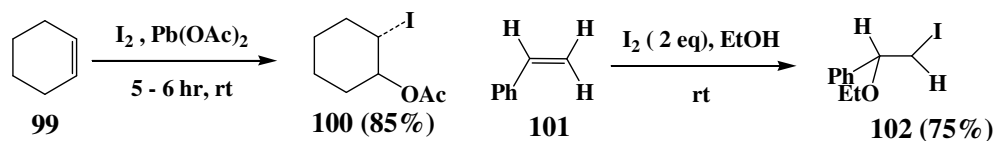
Scheme XVIII



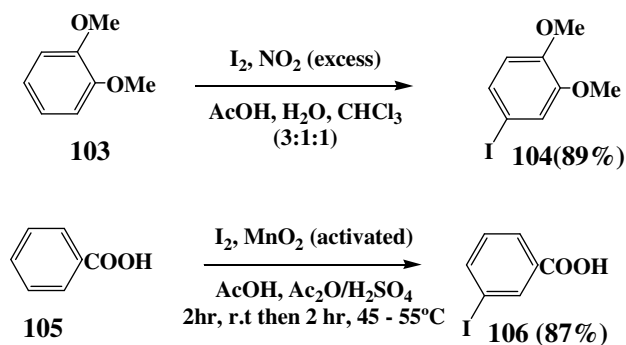
Scheme XIX



Scheme XX



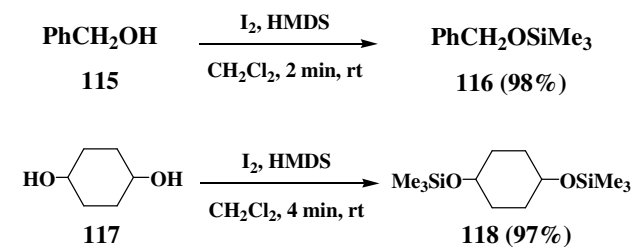
Scheme XXI



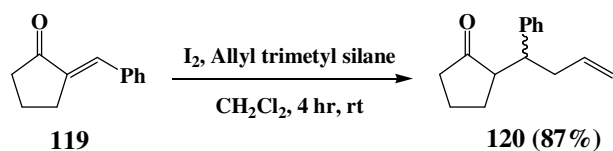
Scheme XXII

aldol product **88** in high yield (Scheme XVIII). Iodine has played an important role in deprotection⁴⁶ of monothioacetal **89-91** and dithioacetal **90-92** (Scheme XIX), in cleavage of t-butyl dimethylsilylether⁴⁷ (OTBDMS) **93-94**, p-methoxybenzyl ether⁴⁸ (OPMB) **95-96** and prenylether⁴⁹ (OPre) **97-98** (Scheme XX). Iodination of double bond⁵⁰⁻⁵² **99-100**, **101-102** (Scheme XXI) and aromatic compounds⁵³⁻⁵⁶ **103-104**, **105-106** (Scheme XXII) has been realized in high yield. The importance of iodine has been recorded in process of deoxygenation^{57,58} of sulphone **107** to **108**, in conversion of various hydroxyphosphonate to trimethylsilyloxyphosphonate **109** to **110** under neutral conditions using HMDS⁵⁹ (Scheme XXIII), to promote O-glycosidation⁶⁰ **111-112** of glycal, C-glycosidation⁶¹ **113-114** (Scheme XXIV) of glycal with allyltrimethylsilane and trimethylsilylation⁶² of a variety of alcohols **115-116** and **117-118** (Scheme XXV).

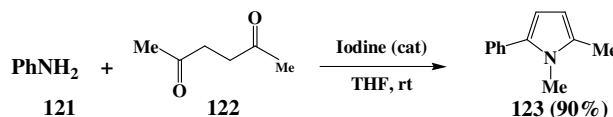
Conjugate addition⁶³ of α , β -unsaturated ketone **119** with allyltrimethylsilane yields adduct **120** (Scheme XXVI) with high selectivity in presence of iodine. Synthesis of substituted pyrrole **123** from amine **121** and hexanedione **122** using iodine-catalyzed modified Paul-Knorr method has recently been published⁶⁴ (Scheme XXVII). 3-Pyroles have also



Scheme XXV



Scheme XXVI



Scheme XXVII

been synthesized by reductive coupling of diaryl-2,2-dicyano ethylenes and aromatic nitrile induced by samarium and iodine⁶⁵. Other uses include molecular iodine published by Wang⁶⁶ and use of iodine in organic synthesis⁶⁷⁻⁶⁹.

Conclusions

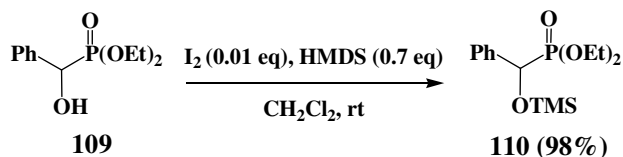
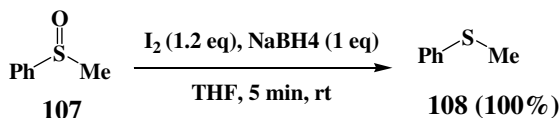
This review focusses the importance of iodine as an effective catalyst for various organic transformations. Although many observations have not received applications in synthesis of natural products or complex structures in details, it is believed that in near future these observations will be useful in synthesis of these compounds. The present review would serve the need of organic chemists engaged in searching new applications of iodine for organic synthesis.

Acknowledgements

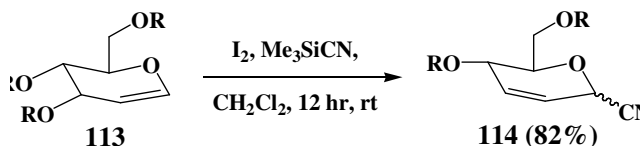
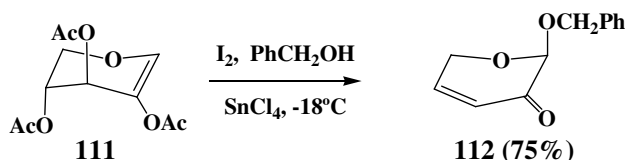
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Scheme XXIII



Scheme XXIV

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