Molecular iodine-mediated α-iodination of carbonyl compounds

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The electrophilic properties associated with iodine have been exploited in recent years to effect α-halogenation of carbonyl compounds and their α,β-unsaturated derivatives. In this review, molecular iodine is presented as a readily-available and easy-to-handle reagent to effect α-halogenation of carbonyl compounds in the presence or absence of catalysts.

Keywords: iodine, α-halogenation, carbonyl compounds, α,β-unsaturated carbonyl compounds

1 Introduction

Various electrophilic iodonium sources such as *N*-iodosuccinimide, iodine chloride or [hydroxy-(*p*-nitrobenzene sulfonyloxy)iodo]benzene have usually been employed for α-iodination of carbonyl compounds.[1–3] However, the use of molecular iodine as an inexpensive, non-toxic and readily available electrophilic reagent to effect α-halogenation of carbonyl compounds and their α,β-unsaturated systems has now received considerable attention in organic synthesis. The applications of molecular iodine in organic transformations as Lewis acid catalyst, electrophile or oxidant have been reviewed in detail before.[4–8] Some relevant examples involving electrophilic iodination of enolisable carbonyl compounds and their α,β-unsaturated derivatives using elemental iodine are included in a recent review by Stavber *et al.*[7] A comprehensive review that focuses primarily on methods that employ iodine in α-iodination of carbonyl compounds and their α,β-unsaturated systems to afford α-iodo- or α,α′-diiodocarbonyl derivatives is thus worth special attention.

2 Methods

2.1 Indirect methods for the *α*-iodination of carbonyl compounds

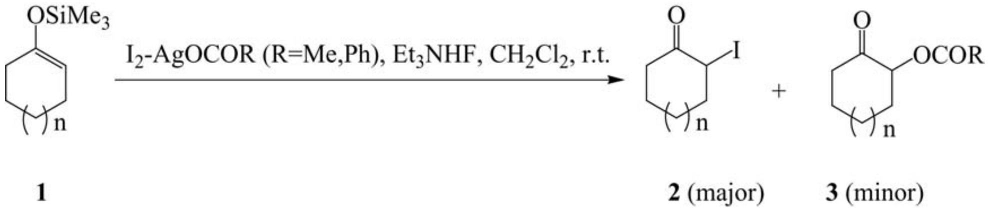
The classical approaches to α-iodoketones involved indirect synthesis from the corresponding bromoketone precursors or through iodination of enol acetates or enol silylethers derived from carbonyl compounds.

2.1.1 α-Iodination of carbonyl compounds through halogen interchange

α-Iodoketones[9] and α-iodocarboxylic acids[10–12] are prepared through halogen interchange of bromo ketones and carboxylic acids with sodium iodide in acetone. However, the reaction is subject to pronounced steric effects. Simple α,α′-diiodoketones such as 1,3-diiodobutan-2-one and 2,4-diiodopentan-3-one were prepared from the corresponding α,α′-dibromoketones *via* halogen exchange with sodium iodide (ref. 13 and references therein). However, the authors did not include the physical data of the prepared compounds and the method was found not to be applicable to cyclic ketones.

2.1.2 Iodination of carbonyl compounds through enol acetates or enol silylethers

This indirect approach to α-iodocarbonyl compounds involves treatment of enol acetates or enol silylethers with silver acetate (AgOCOR) and iodine followed by triethylammonium fluoride (Et_3NHF) or copper(II) nitrate.[14,15] Treatment of enol silyl ethers **1** derived from cycloheptanone (*n*=2), cyclooctanone (*n*=3) and cyclododecanone (*n*=7) with AgOCOR–I_2 (2:1) mixture followed by Et_3NHF previously afforded mixtures of α-iodo- **2** (major) and α-acyloxy-derivatives **3** (minor) (Scheme 1).[15] Rathke and Lindert also reported a convenient method for the synthesis of α-iodoesters involving halogenation of ethyl α-lithioalkanoates with iodine in THF at –78 °C to afford the corresponding ethyl α-iodoalkanoate in 80–95% yield.[16] The use of highly toxic metal acetates or difficulties in the synthesis and purification of enol silylethers presented serious drawbacks for this approach.



Scheme 1 Reaction of enol silyl ethers with AgOCOR–I_2.

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$$\underset{\mathbf{4}}{RCH_2CO_2H} \xrightarrow{I_2,\ CuCl\text{-}CuCl_2.H_2O,\ 120\ ^{\circ}C,\ 6\text{ - }7\ h} \underset{\mathbf{5}}{RCHICO_2H}$$

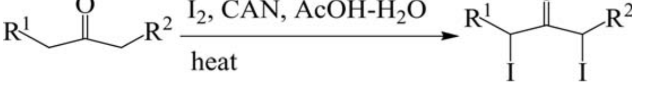
[R=CH_3– (90%), CH_3CH_2– (85%), $CH_3CH_2CH_2$– (85%)]

Scheme 2 Iodine–copper salt mediated iodination of carboxylic acids.

2.2 Direct methods for *α*-iodination of carbonyl compounds

α-Iodination of ketones and carboxylic acids using elemental iodine is generally conducted in the presence of catalytic or stoichiometric amounts of metal-containing reagent under acidic conditions. This approach takes advantage of the large size and high polarisability of molecular iodine, which afford it a dual role as a catalyst that initially promotes enolisation and as a reagent that subsequently reacts with the enol to afford α-iodocarbonyl compounds.[17] Moreover, the HI generated *in situ* during the reaction facilitates enolisation of the carbonyl compound. Consequently, several methods employing molecular iodine without metal catalyst have also been developed in recent years. Harpp *et al.* reacted series of acyl halides with molecular iodine in refluxing thionyl chloride to afford α-iodoacyl chlorides.[18] Thionyl chloride is essential as solvent and reagent to trap the released hydrogen iodide to generate iodine and sulfur and thus facilitate the formation of iodoacyl halides. Iodine-copper(II) acetate mixture in acetic acid was used to convert several ketones into α-iodoketones.[19] However, the drawback with these reaction conditions is the loss of iodine from the reaction as metallic iodide and the problem of lack of regioselectivity when applied to unsymmetrical ketones. Direct α-iodination of carboxylic acids **4** with iodine-copper salts under reflux to yield α-iodocarboxylic acids **5** in good yields was first reported by Horiuchi and Satoh (Scheme 2).[20] The reactivity of copper(I) and copper(II) salts used was found to follow the following trend: CuCl (5 h) > CuOAc (6 h) > $CuCl_2.H_2O$ (13 h) > $Cu(OAc)_2.H_2O$ (40 h).

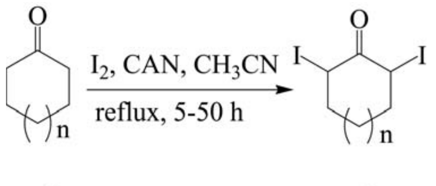
Treatment of ketones with iodine (0.5 equiv.) and cerium(IV) ammonium nitrate (CAN, 0.5 equiv.) in alcohol or acetic acid afforded α-iodoketones in high yields.[21–23] Cerium(IV) ion is believed to coordinate strongly with the carbonyl oxygen leading to enolisation.[23] For unsymmetrical ketones such as hexan-2-one and heptan-3-one in alcohol (methanol, ethanol, propan-1-ol, propan-2-ol) at room temperature, enolisation through C-3 is favoured leading to iodination on the more substituted (C-3) position.[23] Mixed iodinated derivatives (C-1 *versus* C-3) were however observed with higher alcohols at 50 °C. It is believed that at higher temperatures, a cerium(IV)–alcohol complex forms rapidly leading to attack of the ketone by I^+ on the least hindered site (C-1). Horiuchi's group used an iodine–CAN mixture in acetic acid-water (9:1, v/v) under reflux to convert unsymmetrical ketones **6** into the corresponding α,α′-diiodoalkanone derivatives **7** exclusively (Scheme 3).[22] An iodine–CAN mixture in refluxing acetonitrile also converted cycloalkanones **8** into the corresponding α,α′-diiodocycloalkanones **9** (Scheme 4).[22]



6 **7**

	R¹	R²	%Yield	*dl/meso*
7a	Me	Me	62	0/100
7b	H	*n*-Pr	61	–
7c	H	*n*-Bu	82	–
7d	*n*-Pr	*n*-Pr	86	25/75

Scheme 3 Iodination of unsymmetrical ketones using I_2–CAN.



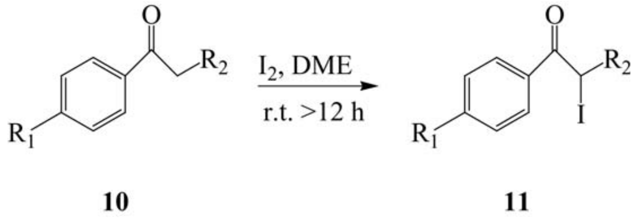
8 **9**

	n	Time/h	Yield/%	*Trans/cis*
9a	1	5	55	67/33
9b	2	6	85	92/8
9c	3	24	50	100/0
9d	7	50	75	0/100 (*meso*)

Scheme 4 Diiodination of cycloalkenones with iodine–CAN mixture.

An iodine–CAN mixture in acetonitrile or aqueous acetic acid provides an efficient method for the synthesis of simple α,α′-diiodoketones and their α,α′-diiodocycloalkanone analogues, which cannot be synthesised through halogen exchange of α,α′-dibromoketones with sodium iodide.[13] Exclusive formation of α-iodoketones is attributed to the formation of a cerium(IV)–alcohol complex, which presumably leaves the α-iodoketone unactivated thus inhibiting further enolisation, hence the reaction stops at monoiodination. Formation of a cerium(IV)–solvent complex is probably not possible in acetonitrile or aqueous acetic acid and in this case cerium(IV) ions coordinate strongly with the carbonyl group of the incipient α-iodocarbonyl derivative to facilitate enolisation and subsequent iodination to afford an α,α′-diiodinated ketone.

In another development, carbonyl compounds were reacted with an iodine–mercury(II) chloride mixture in an acidic medium to afford iodinated derivatives.[24] However, this method, which makes use of environmentally unfriendly mercury was found not to be applicable to cyclic ketones. A mild and effective protocol involving α-iodination of ketones using molecular iodine activated by 30% aqueous hydrogen peroxide in the presence of an acid catalyst was reported.[25] According to these authors, attempted iodination of acetophenone with iodine in diethyl ether, chloroform or ethanol at room temperature failed. It was however established that both cyclic and acyclic aliphatic ketones undergo α-iodination with molecular iodine and 30% hydrogen peroxide mixture (1:1.2 equiv) in refluxing methanol catalysed by concentrated sulfuric acid or dodecatungstosilic acid hydrate ($H_2SiO_4.12WO_3.26H_2O$) to afford α-iodinated ketones in high yields.[25] Interestingly, when Rao and Jadhav employed iodine (2–4 equiv.) in dimethoxyethane (DME) on cyclic and acyclic ketones in the absence of any catalyst or potentially explosive hydrogen peroxide they isolated the corresponding α-iodinated carbonyl derivatives exclusively.[17] Reaction of acetophenone derivatives **10** with iodine in DME afforded the corresponding α-iodinated



	R_1	R_2	Yield/%
11a	H	H	74
11b	H	Me	90
11c	H	CH_3CH_2	86
11d	H	$CH_3CH_2CH_2$	87
11e	Me	H	81
11f	Br	H	77
11g	MeO	H	62
11h	C_6H_5	H	74
11i	HO	H	64

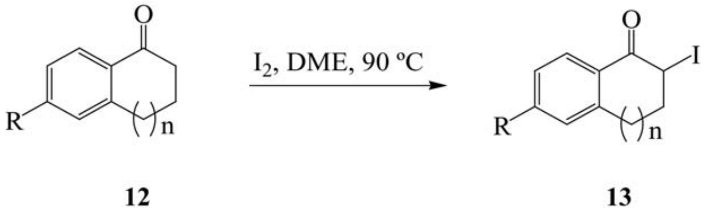
Scheme 5 iodination of acetophenone derivatives using iodine in DME.

derivatives **11** in 62–90% yields (Scheme 5).

The neutral conditions involving I_2 in DME were also used to convert tetralone derivatives **12** (*n*=1) and indan-1-one **12** (*n*=2) into the corresponding α-iodinated derivatives **13** in high yields (Scheme 6).[17] The use of an I_2–DME mixture for α-iodination of cyclic and acyclic aliphatic ketones avoids the application of costly and difficult to handle metal or acid catalysts, CAN or peroxides. However, I_2 in DME was found not to be selective for unsymmetrical alkyl ketones **14** and to afford mixtures of α-iodoketones **15–17** with the 3-iodo isomer **15** as the major product (Scheme 7).[17] The problem of selectivity to form either the 3-iodo isomers **15** or α,α′-diiodo derivatives **17** can be circumvented by the use of an iodine–CAN mixture in alcohols [21–23] or acetonitrile,[22] respectively.

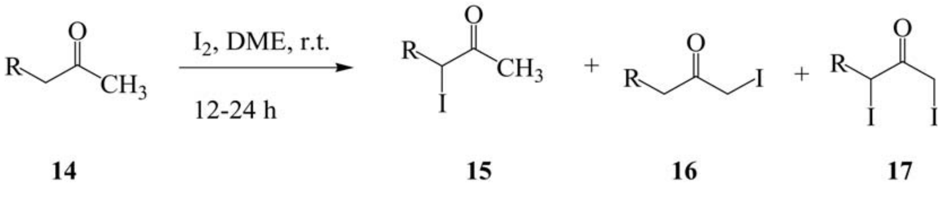
Several derivatives of indan-1-one and 3,4-dihydronaphthalen-1(2*H*)-one (2 equiv.) bearing a hydroxyl or a methoxy substituent on the aromatic ring were iodinated exclusively at the α-carbon using iodine (1.1 equiv.) activated by 1.1 equivalent of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) [Selectfluor®] in methanol.[26] The use of a stoichiometric amount of relatively costly Selectfluor® makes I_2–DME a reagent mixture of choice particularly for acid or base sensitive substrates. In another development, iodine (0.55 equiv.) and powdered SeO_2 (0.55 equiv.) in acetic acid or acetonitrile were employed to effect α-iodination of chromanone and tetralone derivatives **18** to afford the corresponding α-monoiodinated tetralone and chromanone derivatives **19** (Scheme 8).[27] The drawback with these reaction conditions is the use of a stoichiometric amount of environmentally unfriendly selenium oxide and the harsh acidic conditions involved.

Goswami and co-workers employed molecular iodine and oxone® (a stable ternary mixture of $KHSO_5/KHSO_4$ and K_2SO_4 in a 2:1:1 molar ratio) as catalyst to effect selective α-iodination of cyclic ketones such as tetralone, cyclopentanone, cyclohexanone and cyclodecanone to afford within 3 minutes the corresponding monoiodo derivative in 91%, 96%, 96% and 93% yield, respectively.[28] Since iodine is completely consumed into the organic molecules in the absence of solvent with no need for tedious work-up and purification requirements, this methodology represents a suitable alternative to the use of I_2-DME, I_2-SeO_2 or I_2–CAN mixture. Iodine–oxone® mixture at room temperature was also found to effect selective α-iodination of a series of 1,3-dicarbonyl compounds **20** (1,3-diketones, β-ketoesters and diethyl malonate) within 2–3 minutes to afford mono-iodo derivatives **21** in excellent yields (Scheme 9).[28] Iodinated 1,3-dicarbonyl derivatives would probably decompose during aqueous work or purification by column chromatography and have yet to be synthesised using the other reagents described above.



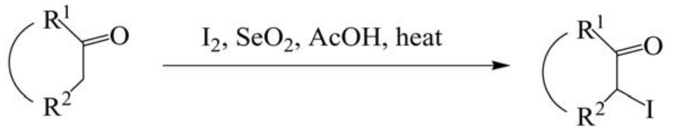
[*n*=1, R=H (94%); *n*=1, R=MeO (81%); *n*=0, R=H (77%)]

Scheme 6 Molecular iodine–promoted α-iodination of 1-tetralones and 1-indanone.



	Ketone	I_2 /equiv.	Yield/%	**15:16:17** (^{1}H NMR)
a	Nonan-2-one	4	66	89:11:0
b	Nonan-2-one	2	59	84:12:4
c	Nonan-2-one	3	82	85:3:12
d	Octan-2-one	2	30	95:2:3
e	Octan-2-one	3	69	81:7:12
f	Octan-2-one	4	48	82:4:14
g	Benzyl acetone	2	37	90:3:7
h	Benzyl acetone	3	49	84:2:14

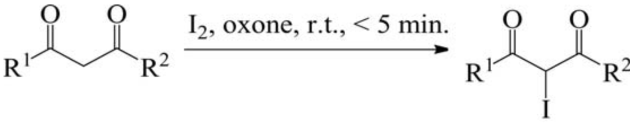
Scheme 7 Iodination of unsymmetrical alkyl ketones using I_2 in DME.



18

19 (R^1=R^2=alkyl; R^1=R^2=cycloalkyl)

Scheme 8 I_2–SeO_2–mediated α-iodination of chromanone and tetralone derivatives.



20

21

	R^1	R^2	Yield/%
21a	Me	OMe	96
21b	Me	OEt	93
21c	Me	$OC(Me)_3$	91
21d	Me	OCH_2Ph	90
21e	Ph	OEt	92
21f	Me	Allyl	88
21g	Me	Me	92
21h	Me	Ph	94
21i	Ph	Ph	95
21j	OEt	OEt	94

Scheme 9 Iodine–oxone®–mediated iodination of 1,3-dicarbonyl compounds.

2.3 *α*-Iodination of heteroatom-containing carbonyl compounds

2.3.1 Selective α-iodination of heterocyclic systems

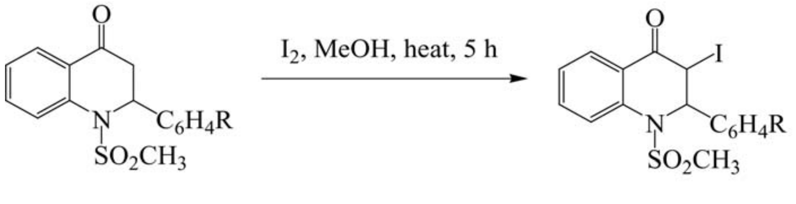
Selective halogenation of heterocyclic systems continues to attract considerable attention because of the profound effect the introduction of a halogen atom into the heterocyclic ring can have on the physical, chemical and biological properties of such systems. Regio- and stereo-selective α-iodination of 2-aryl-1-methylsulfonyl-2,3-dihydroquinolin-4(1*H*)-ones **22** was effected using iodine in refluxing methanol to afford the corresponding 2-aryl-3-iodo-1-methylsulfonyl-2,3-dihydroquinolin-4(1*H*)-ones **23** (Scheme 10).[29] The advantage of this methodology is the use of readily available and easy-to-handle reagents and the ease of isolation of products.

2.3.2 α-Iodination of α,β-unsaturated cyclic carbonyl compounds

The α-haloenones derived from α,β-unsaturated carbonyl compounds provide an important functional group that could facilitate metal-catalysed C–C bond formation.[30–35] Direct α-iodination of substituted cycloalkenones with iodine and pyridine in carbon tetrachloride was first reported by Johnson *et al.*[36] and since then several C-3 iodinated flavone and thioflavone analogues have been prepared following this strategy or modification thereof.[30,32,34] Treatment of 8-isobutyl-5,6,7-trimethoxy-2-methyl-4*H*-chromen-4-one with iodine in the presence of silver trifluoroacetate (CF_3CO_2Ag), for example, afforded the 3-iodochromen-4-one derivative in 95% yield.[30] Silver salts are difficult to dispose of and the generality of this reaction has not been demonstrated.

An iodine-bis(trifluoroacetoxyiodo)benzene (BTI) mixture converted 2-(4-methylthiophenyl)-4*H*-1-benzopyran-4-one into the 3-iodobenzopyran-4-one derivative.[32] In another development, an I_2–CAN mixture was employed to effect C-3 iodination of 2-arylchromones and thioflavone analogues to afford the corresponding 3-iodo derivatives in 24–80% and 95–98%, respectively.[37] This reagent mixture was also employed by Pal *et al.* to effect direct iodination of 2-(3,4-dimethoxyphenyl)chromenon-4(4*H*)-one and its 5-nitro derivative.[38] The resulting 2-aryl-3-iodochromen-4(4*H*)-ones were employed for the synthesis of 3-alkynyl derivatives *via* palladium(0)–copper iodide catalysed Sonagashira cross-coupling in aqueous media.[38] An iodine–Na_2CO_3 mixture in THF at room temperature was found to effect C-3 iodination of 2-arylquinolin-4(1*H*)-ones **24** to yield the corresponding 2-aryl-3-iodoquinolin-4(1*H*)-ones **25** in reasonable yield (83–90%) and high purity (Scheme 11).[34] An alternative procedure which makes use of I_2–CAN mixture in acetonitrile at 70–80 °C to afford 2-aryl-3-iodoquinolin-4(1*H*)-ones has also been reported.[35] Mild reaction conditions associated with I_2-Na_2CO_3 in tetrahydrofuran (THF) and the ease of separation of 2-aryl-3-iodoquinolin-4(1*H*)-ones make this methodology a more suitable choice than the I_2–CAN mixture procedure which involves relatively harsh conditions. The 2-aryl-3-iodoquinolin-4(1*H*)-ones are suitable candidates for palladium-catalysed Suzuki[34] and Sonagashira reactions[35] to afford polysubstituted and annulated quinoline derivatives, respectively.

Several cycloalkenone derivatives **26** substituted with an *O*- or *N*-containing substituent at the 3-position were iodinated under neutral conditions using iodine in dimethylformamide (DMF) or acetonitrile to afford **27** in high yields (Scheme 12).[39] Kim and coworkers, on the other hand, employed iodine (1 equiv.) in the presence of triethylamine to convert a series of enaminones **28** into α-iodo enaminones **29** within 5 minutes and in excellent yields (Scheme 13).[40] Advantages of this

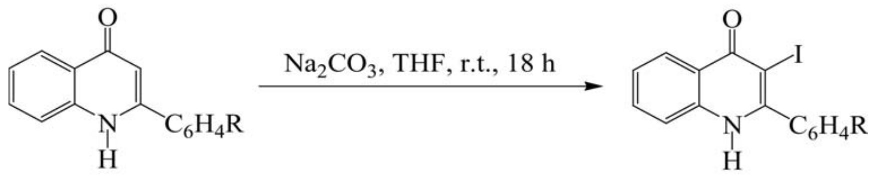


22

23

4-R=H (60%), F (50%), Cl (58%), Br (55%), OMe (90%)

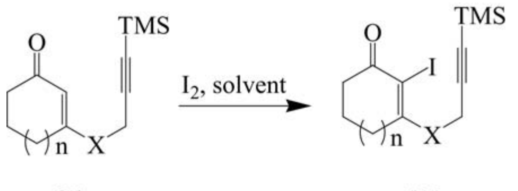
Scheme 10 I_2–MeOH–promoted C-3 iodination of 2-aryl-1-methylsulfonyl-2,3-quinolin-4(1*H*)-ones.



24 **25**

4-R=H (85%), F (83%), Cl (90%), OMe (83%)

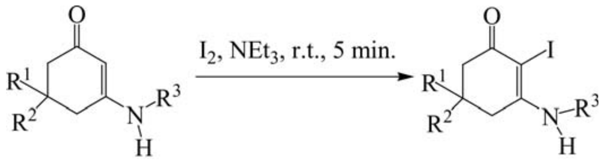
Scheme 11 I$_2$–promoted C-3 iodination of flavone analogues.



26 **27**

	N	X	Solvent	Yield/%
27a	0	O	DMF	88
27b	1	O	DMF	85
27c	0	NH	CH_3CN	90
27d	1	NH	CH_3CN	95

Scheme 12 α-Iodination of 3-heteroatom-substituted cycloalkenone derivatives.



28 **29**

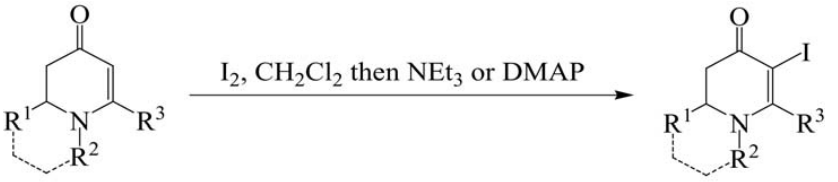
	R^1,R^2	R^3	Yield/%
29a	H,H	C_6H_5	95
29b	H,H	4-ClC_6H_4	93
29c	H,H	PhCH_2	96
29d	H,H	Cyclohexyl	94
28e	Me,Me	C_6H_5	91
29f	H,Me	C_6H_5	96
29g	H,Ph	C_6H_5	92

Scheme 13 Iodination of enaminones using iodine in triethylamine.

method are short reaction times and excellent yields. However, it may not be adaptable for base-sensitive substrates. α-Iodination of 5,6-disubstituted cyclohexenone derivatives with iodine was successfully promoted by 4-(dimethylamino)pyridine (DMAP) in dichloromethane instead of pyridine which resulted in half conversion.[41] Perhaps, iodine–oxone® mixture previously employed for selective α-iodination of 1,3-dicarbonyl compounds[28] could be employed in this case to avoid the use of basic conditions involving pyridine or DMAP.

Wang and coworkers in their study of microwave-assisted Suzuki–Miyaura couplings prepared α-iodoenaminones **31** in 85–99% yield from the corresponding enaminones **30** using iodine in the presence of a tertiary amine in dichloromethane (Scheme 14).[42]

Plisson and Chenault employed iodine and potassium carbonate in DMF on 7-methyl[1,8]naphthyridin-4(1*H*)-one to afford 3-iodo-7-methyl[1,8]naphthyridin-4(1*H*)-one in 82% yield.[43] The Johnson strategy[36] or its modification[30,32,34] which employs iodine in the presence of amine or inorganic base for the α-iodination of α,β-unsaturated carbonyl compounds represent suitable alternatives to the use of relatively expensive and environmentally unfriendly oxidants such as CAN, silver trifluoroacetate or bis(trifluoroacetoxyiodo)benzene.



30 **31**

	R^1,R^2	R^3	Yield/%
31a	$CH_2CH_2CH_2$	H	99
31b	$CH_2CH_2CH_2CH_2$	H	97
31c	$CH_2CH_2CH_2CH_2$	Ph	85
31d	H,H	CH_3	88
31e	H,H	CH_2Ph	85
31f	CH_2Ph,H	H	94

Scheme 14 α-iodination of enaminone derivatives with iodine in the presence of a base.

3 Conclusions

Although metal catalysed iodination is a well-established procedure, harsh acidic conditions and the difficulty in disposing of environmentally unfriendly metal salts are serious drawbacks associated with these methods. Iodine has established itself as an efficient, readily available and easy-to-handle electrophilic reagent to effect direct α-halogenation of carbonyl systems in the presence or absence of oxidising agents. Molecular iodine owes its iodination potential to its dual role as a catalyst that initially promotes enolisation and as a reagent that subsequently reacts with the enol to afford α-iodocarbonyl compounds. Moreover, the applications of iodofunctionalised systems in carbon–carbon and carbon–heteroatom bond-forming reactions owe their versatility to the ability for iodine to facilitate carbon–carbon bond formation and metal exchange (Suzuki, Sonogashira, Heck, *etc*.) reactions.

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