Review

Electrophilic Iodination of Organic Compounds Using Elemental Iodine or Iodides: Recent Advances 2008–2021: Part I

Njomza Ajvazi [1,*] and Stojan Stavber [1,2]

[1] Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia; stojan.stavber@ijs.si
[2] Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[*] Correspondence: njomza.ajvazi@rezonanca-rks.com; Tel.: +386-44-258-553

Abstract: The iodination of organic compounds is of great importance in synthetic organic chemistry. It opens comprehensive approaches for the synthesis of various biologically active compounds. The recent advances in iodination of organic compounds using elemental iodine or iodides, covering the last thirteen years, are the objective of the present review.
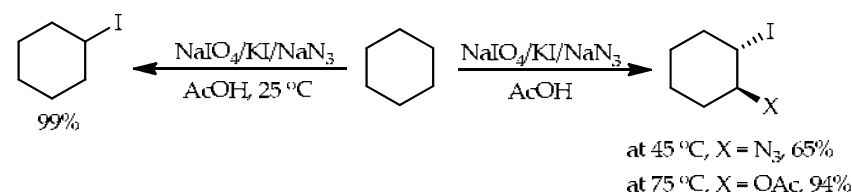
1. Introduction

The introduction of iodine as an available, inexpensive, environmentally friendly element into organic molecules has attracted a significant interest providing versatile building blocks in synthetic organic chemistry [1]. Iodine compounds have widespread use in organic chemistry. Iodinated compounds are frequently used as reagents in organic synthesis [2]. The best choice for the iodination of organic compounds is the use of molecular iodine or the iodide anion in combination with environmentally friendly and atom-efficient oxidants in the presence of desirable solvents or under solvent-free protocols, thus enhancing the green chemical profile of the iodination process [3]. Molecular iodine is extensively employed for α-iodination of alkyl carbonyl compounds [4]. It could act as a catalyst promoting enolisation and as a reagent reacting with enol to afford α-iodocarbonyl compounds [5]. Comprehensive synthetic protocols for electrophilic iodination of organic compounds employing I_2 or I^- were reviewed by Stavber and co-workers in 2008 [6]. The reports covered by this review [6] mainly carried low green chemical profiles, thus challenging greener-related protocols. Thus, in the present review, as part I of the matter, related protocols have been elaborated to highlight recent advances in the iodination of organic compounds, including alkanes, alkenes, alkynes, and alkyl carbonyls using elemental iodine or iodides, covering the period from 2008–2021.

2. Iodination of Alkanes

In 2008, Sudalai and co-workers [7] presented $NaIO_4/KI/NaN_3$ an efficient system for mono- and 1,2-difunctionalization of hydrocarbons through activation of C-H bond, providing vicinal azido- and acetoxy iodinations of cyclic hydrocarbons in high yields (Scheme 1). This protocol is successful for acyclic and cyclic alkanes.

Scheme 1. C-H activation of cyclohexane mediated by $NaIO_4$.

Homolytic cleavage of I-N$_3$ gives an azide radical, which removes a proton from cyclic alkane to provide an alkyl radical. The reaction of an alkyl radical with I$_2$ provides alkyl iodide followed by oxidative elimination giving alkene, which undergoes addition of either I-N$_3$ or I-OAc across the double bond (Scheme 2).
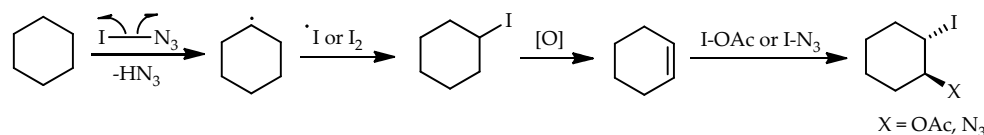
Scheme 2. Plausible reaction pathway.

In 2012, Yu and co-workers [8] reported diastereoselective C-H iodination with *i*-Pr- and *t*-Bu-substituted oxazoline auxiliaries catalyzed by palladium (II) (Scheme 3).

R^1 = R^2 = *t*-Bu, 83% yield
R^1 = Et, R^2 = *t*-Bu, 91% yield
R^1 = Et, R^2 = *i*-Pr, 15% yield
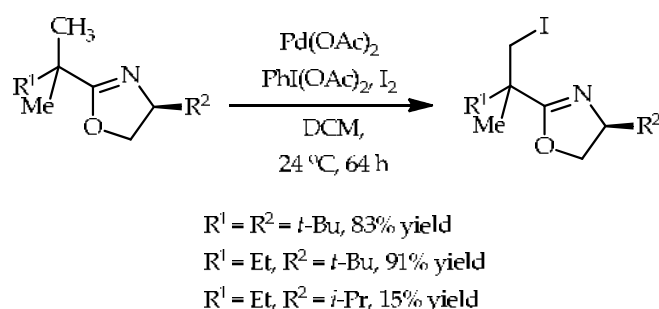
Scheme 3. Diastereoselective C-H iodination *i*-Pr- and *t*-Bu-substituted oxazoline auxiliaries catalyzed by Pd (II).

Zhu and co-workers [9] have presented quinoline-based ligand-enabled palladium (II)-catalyzed iodination of various α-hydrogencontaining carboxylic acid and amino acids (Scheme 4).
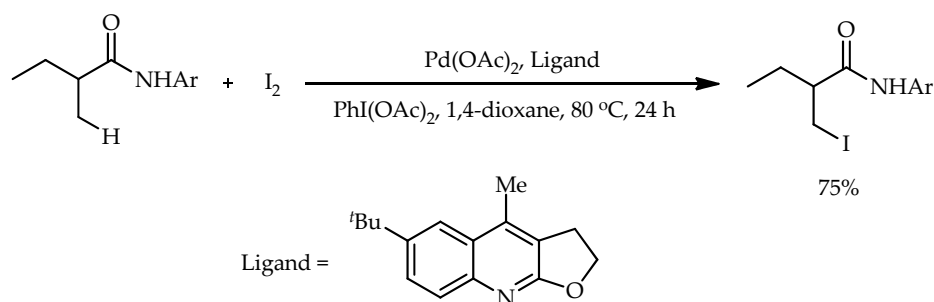

**Scheme 4.** C(sp^3)-H Iodination of carboxylic acid derivatives.

3. Iodination of Alkenes and Alkynes

The considerably breakthrough in the field of electrophilic iodination of alkenes was achieved already in 2005 [10], where, 30% aqueous H$_2$O$_2$ was used as the oxidant for the iodotransformation. However, later in 2008, Stavber and co-workers [11] even improved the green chemical profile of the reaction establishing an environmentally friendly methodology for aerobic oxidative iodination of alkenes using potassium iodide as iodine source catalyzed by sodium nitrite in acidic media providing the corresponding products in good to quantitative yields (Scheme 5). The authors have reported that the alkene was added as the last reactant to avoid polymerization. Moreover, in the case of phenyl-substituted alkynes (phenylethyne) using MeCN as the solvent, the formation of (*E*)-1,2-diiodo-1-phenyl-1-ethene was observed while, in the case of phenyl-1-propyne, a small
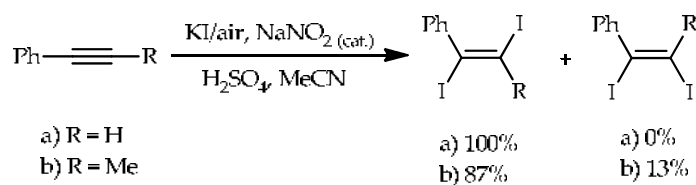
amount of (*Z*)-1,2diiodophenylethene was also obtained (Scheme 6). The presence of an external nucleophile was observed to be beneficial for efficient and selective reactions.


Selected products:

R^1 = H, 93%
R^2 = Et, 42%

R^1 = H, 82%
R^2 = Et, 75%

R^1 = H, 91%
R^2 = Et, 88%
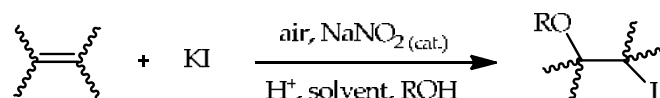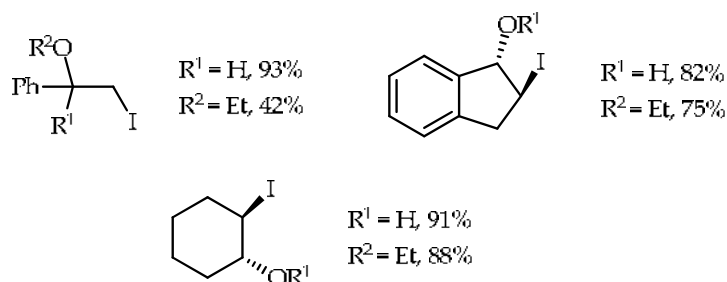
Scheme 5. Aerobic oxidative iodination of alkenes.

a) R = H
b) R = Me

a) 100%
b) 87%

a) 0%
b) 13%

Scheme 6. Aerobic oxidative iodination of phenyl-substituted alkynes.

Huang and Yang [12] have reported a novel and efficient method for synthesizing iodocyclopropylmethanol and 3-iodobut-3-en-1-ol derivatives via the iodohydroxylation of alkylidenecyclopropanes with I_2/H_2O system affording ring-opening or ring-keeping products in moderate to excellent yields (Scheme 7).

Ar = *p*-MeOC₆H₄, 48%,
Ar = *p*-EtOC₆H₄, 31%,

Ar = *p*-MeOC₆H₄, 91%,
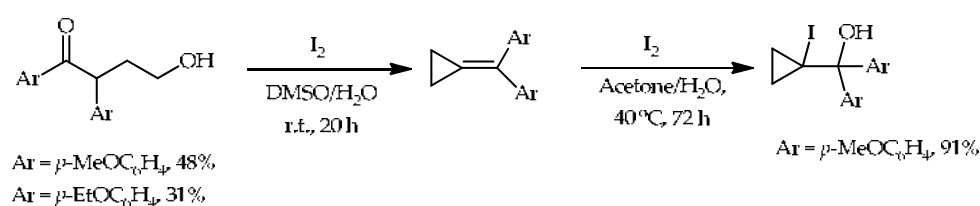
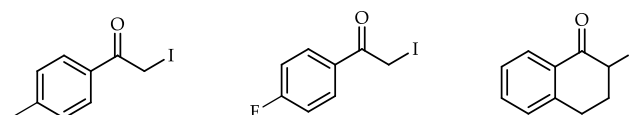**Scheme 7.** Iodohydroxylation of alkylidenecyclopropanes with substituted aromatic rings.

A convenient and eco-friendly method for the synthesis of α-iodoketones from alkenes and alkynes has been reported by Yadav and co-workers [13] using 2-iodoxybenzoic acid (IBX)/I_2 as the effective reagent system in water providing the corresponding products in good to high yields (Scheme 8).

The authors reported that the interaction between alkene and iodine could generate a cyclic iodonium ion, which reacts with water to provide an iodohydrin. The iodohydrin reacts with IBX to afford α-iodoketone (Scheme 9).
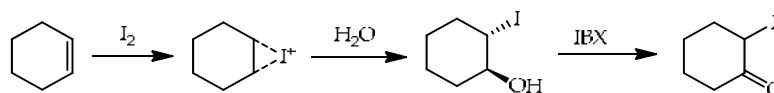
An efficient and facile protocol for the iodomethoxylation and iodohydroxylation of alkenes and alkynes in the presence of *m*-iodosylbenzoic acid as a recyclable reagent has been achieved by Chi and co-workers [14] (Scheme 10).
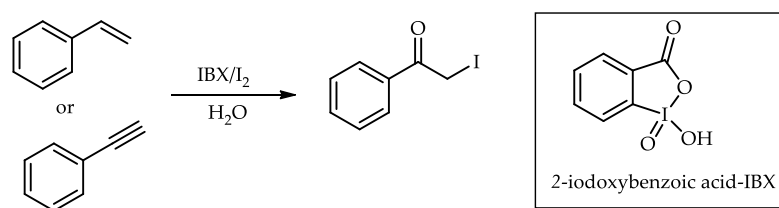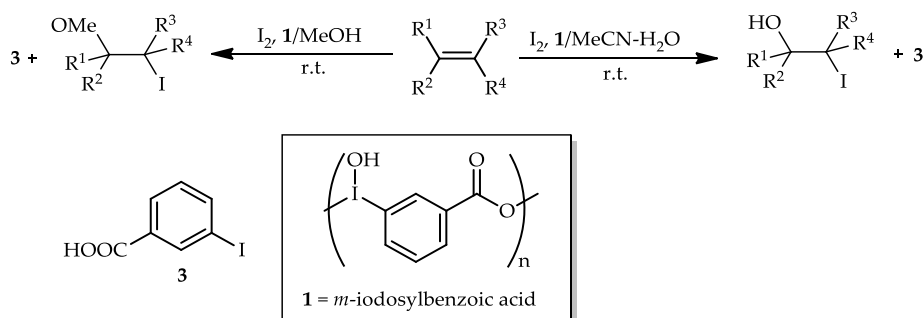
Selected products: 78–87% yields.

Scheme 8. Iodination of alkenes and alkynes mediated by IBX/I_2.
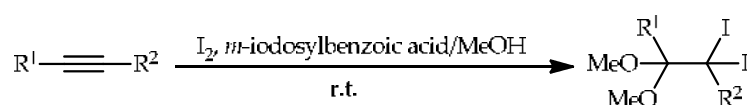

Scheme 9. Possible reaction pathway.

Scheme 10. Iodomethoxylation and iodohydroxylation of alkenes.

In the case of performing the reactions between alkynes and I_2/*m*-iodosylbenzoic acid/MeOH diiododimethoxylation products were obtained (Scheme 11).

Selected products:
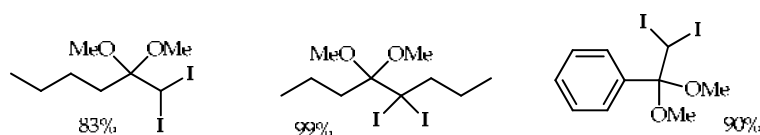
Scheme 11. Diiododimethoxylation of alkynes.

By treatment of the reaction mixture with an anionic exchange resin, pure iodo-functionalized products were provided. Unreacted *m*-iodosylbenzoic acid and reduced *m*-iodobenzoic acid are regenerated from the resin by treatment with HCl.

A simple, efficient, and practical method for the iodination of alkynyl enolates has been described using allenoates as the starting material through an alkynyl enolate as the intermediate. The reaction of the silyl ether of alkynyl enolate with iodine provides

iodoallenoate in good yield [15]. Grigg and co-workers [16] developed a protocol for the synthesis of 1-C-(tetra-O-acetyl-β-D-galactopyranosyl)-2,3-diiodo-1-propene using β-C-galactose allene as a starting material with iodine in the presence of ethanol as a solvent (Scheme 12).
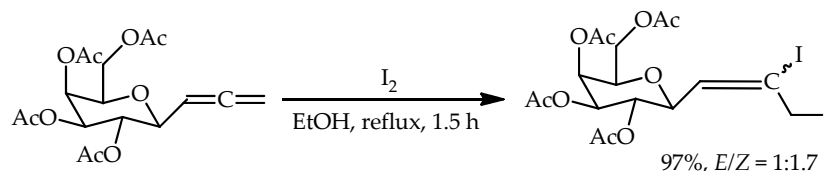
Scheme 12. The reaction of β-C-galactose allene with I_2.

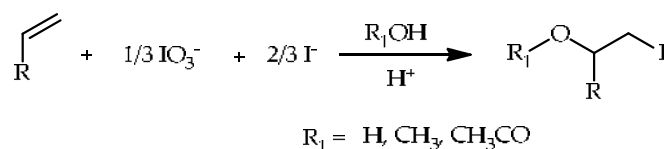A convenient method for synthesizing of vicinal halohydrins, haloacetates, and halo methyl ethers from olefins with 2:1 I^-/IO_3^- has been described [17]. Iodo reagent was found to be better for reaction with linear alkenes and the elimination of diiodo impurity (Scheme 13). I^-/IO_3^- was not successful for the vicinal functionalization of chalcones and stilbene.

Selected products:
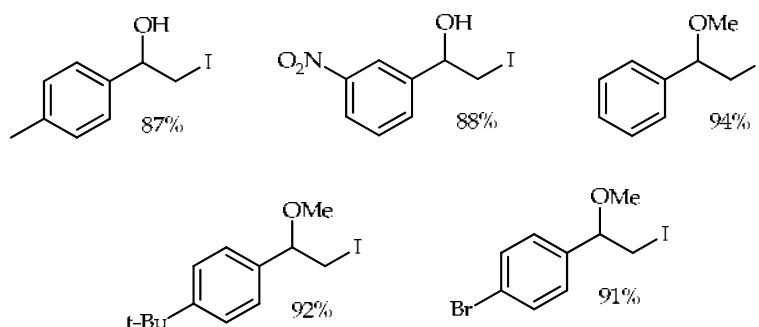
Scheme 13. Vicinal functionalization of alkenes with 2:1 I^-/IO_3^- reagents.

Iodofluorination of electron-deficient olefins such as α,β-unsaturated esters, phosphonate, and amides with iodonium cation species generated by the anodic oxidation of iodide anion in Et_3N-5HF/$MeNO_2$ has been reported [18], providing the corresponding iodofluorinated products in good to moderate yields (Scheme 14).
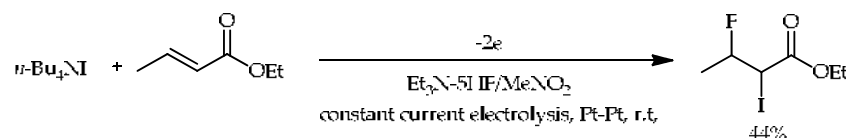
Scheme 14. Electrochemical iodofluorination of α,β-unsaturated esters.

An efficient route for the aerobic photo-oxidative synthesis of phenacyl iodides from styrenes, H_2O and I_2 has been reported by Itoh and co-workers [19], providing the corresponding products in moderate to high yields (Scheme 15).
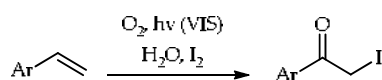
Scheme 15. Photo-oxidative synthesis of phenacyl iodides using I_2.

A simple and efficient method for azidoiodination of alkenes has been reported by Sudalai and co-workers [20] using $NaIO_4/KI/NaN_3$ combination. Through an anti-Markovnikov fashion, the regiospecific 1,2-azidoiodination proceeds to give β-iodoazides in quantitative yields (Scheme 16).

Scheme 16. Azidoiodination of alkenes mediated by $NaIO_4/KI/NaN_3$ system.

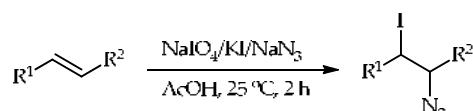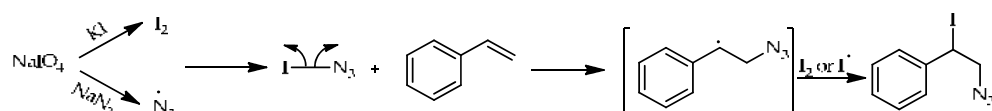$NaIO_4$ oxidizes both KI and NaN_3 to release I_2 and an azide radical, a combination of which gives IN_3. Homolysis of IN_3 affords an azide radical, which reacts with alkenes to form alkyl radical species. The combination of an alkyl radical with either molecular iodine or iodine radical affords β-iodoazides (Scheme 17).

Scheme 17. Plausible reaction mechanism.

Hanessian and co-workers [21] developed a method for the total synthesis of Jerangolid A (shows antifungal activity) where I_2 was used for iodination of lactone in the presence of pyridine in DMF underwent further steps. Kuhakarn and co-workers [22] have described the method for the direct synthesis of β-keto sulfones between the reaction of sodium arensulfinates with alkenes, including styrene derivatives, and aliphatic alkenes mediated by *o*-iodoxybenzoic acid/iodine (IBX/I_2) (Scheme 18).
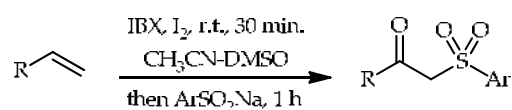
Scheme 18. Synthesis of Keto Sulfones mediated by IBX/I_2.

A new route for synthesizing of 5-hydroxypyrrolin-2-one derivatives from the modified Morita-Baylis-Hillman (MBH) adducts through CuI- mediated aerobic oxidation, allylic iodination, hydration of nitrile, and lactamization has been reported [23].

Krasutsky and co-workers [24] have reported the method for electrophilic monoiodination of terminal alkenes (Scheme 19).
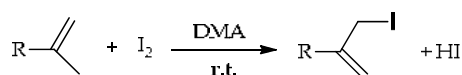
Scheme 19. Monoiodination of terminal alkenes.

The use of the oxidative system (*t*-BuOCl + NaI) as an efficient oxidant and N-iodinating reagent with triflamide and cyclic dienes in acetonitrile for providing 1,1,1-trifluoro-N-((1R,5R)-5-iodocyclopent-2-en-1-yl)methanesulfonamide in low yield has been reported by Shainyan and co-workers [25]. A co-iodination method for alkenes with

(diacetoxyiodo)benzene (DAIB) and I_2 combination and different nucleophilic sources (MeCN-*nucleophile*) providing the corresponding products in moderate to high yields have been reported [26] (Scheme 20).

Selected products:
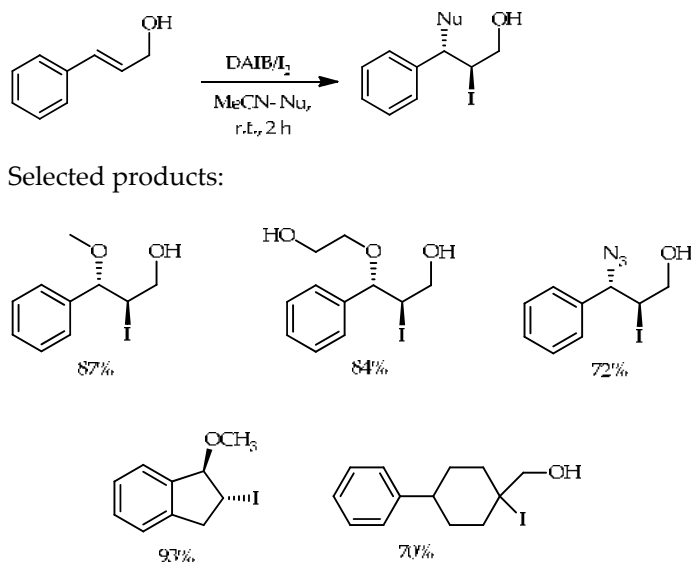
Scheme 20. Co-Iodination of cinnamyl alcohol derivatives and alkenes.

Ma and co-workers [27] established stereoselective iodohydroxylation of 1,2-allenylic sulfoxides using iodine and benzyl thiol, providing 3-hydroxy-2-iodo-2(*E*)-alkenyl sulfides in the presence of MeCN/H_2O as a solvent.

[Bis(trifluoroacetoxy)iodo]benzene (PIFA) was used as a mediator for ethoxyiodination of enamides with potassium iodide, providing the corresponding products in good to quantitative yields [28]. A convenient method for the synthesis of vicinal iodohydrins and iodoesters from olefins has been reported by Narender and co-workers [29] via $NH_4I$ and oxone system in MeCN/H_2O and DMF/DMA, under catalyst-free at room temperature, providing the corresponding products in good to quantitative yields. This protocol is realizable to various olefins, such as a terminal, symmetrical, and 1,2-disubstituted unsymmetrical olefins. Additionally, 1,2-disubstituted olefins provided excellent diastereoselectivity (Scheme 21).
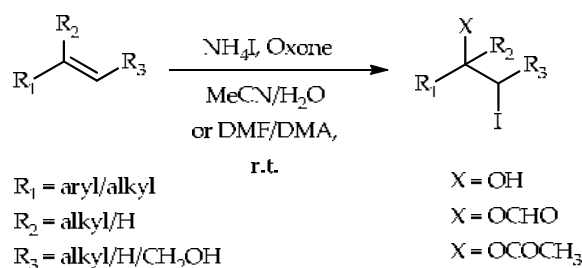
Scheme 21. Vicinal functionalization of olefins via NH_4I/oxone system.

The protocol for the synthesis of iodovinylnaphthols using molecular iodine in the presence of MeCN as the solvent has been developed by Kumar and co-workers (Scheme 22) [30].

Since halohydrins are essential building blocks in organic synthesis and could be transformed to other organic intermediates such as amino-, azidoalcohols, and epoxides, Ning and co-workers [31] established an efficient protocol of iodohydroxylation of olefins with DMSO (dimethylsulfoxide) as an oxidant, an oxygen source, a solvent and HI generated in situ. It was reported that DMSO could oxidize haloanions to halocations under acidic conditions (Scheme 23).
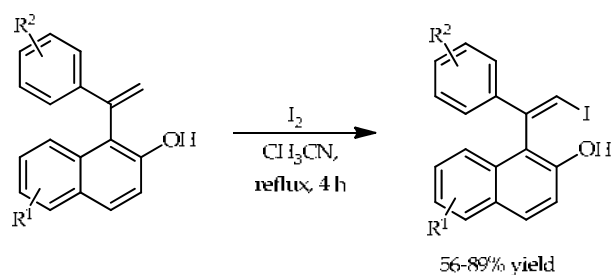
Scheme 22. Vinylic iodination of *ortho*-vinylnaphthols with I_2.
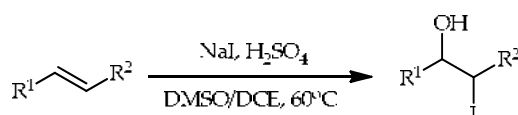
Selected products:
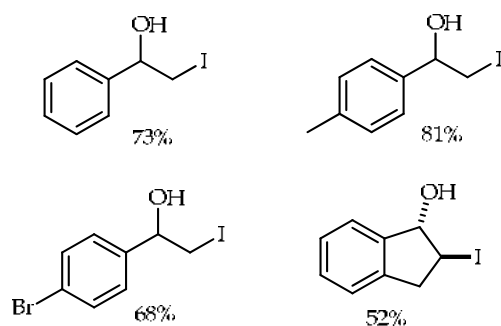
Scheme 23. Iodohydroxylation of olefins with NaI.

Zhu and co-workers [32] developed a one-pot and non-metal strategy for the direct vicinal difunctionalization of alkenes using iodine and *tert*-butyl hydroperoxide (TBHP) to synthesize 1-(*tert*-butylperoxy)-2-iodoethanes in good to high yields (Scheme 24). The method is realizable in the fields of organic synthesis, pharmacology, and medicinal chemistry.

R = alkyl, aryl
R^1 = alkyl, aryl, H
R^2 = alkyl, H
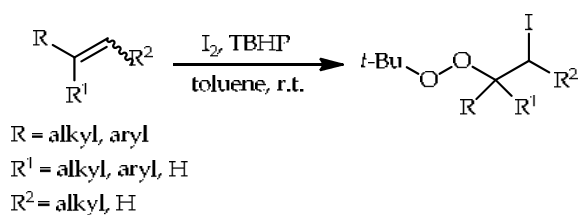
Scheme 24. Synthesis of 1-(*tert*-butylperoxy)-2-iodoethanes with I_2/TBHP.

Iodine monoacetate as an effective reagent was used for the regio- and diastereoselective iodoacetoxylation of alkenes and alkynes. An inexpensive, non-metal, and environmentally friendly protocol for synthesizing iodine monoacetate was presented using iodine and oxone in acetic anhydride and acetic acid combination. It was shown that the reactions with styrene derivatives were more successful than allylic and aliphatic olefins, where regioisomeric mixtures in lower yields were observed (Scheme 25). Additionally, alkynes provided mono- and diiodinations in comparable yields [33].

R = alkyl, aryl, heteroaryl
R' = alkyl, aryl, Br, H
R" = alkyl, CO$_2$Et, COPh, CN, H
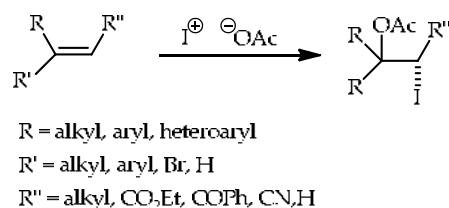
Scheme 25. Oxyiodinations of alkenes with iodine monoacetate.

Liu and co-workers [34] developed the environmentally friendly method for the iodofunctionalization of olefins using I$_2$O$_5$ as the inorganic oxidant and LiI as the iodine source, in H$_2$O/acetone as the green solvent, providing the iodinated products in good to excellent yields (Scheme 26). The synthesis of different medicinal and agrochemical products could be realized through this method.
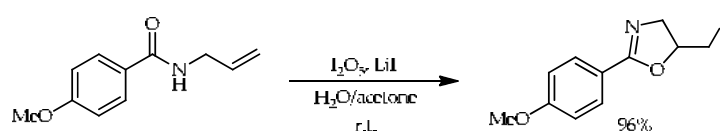
Scheme 26. Iodofunctionalization of olefins using I$_2$O$_5$/LiI.

It is assumed that I$_2$O$_5$ oxidizes LiI to form HOI, which acts as a reactive electrophilic intermediate to cause the electrophile-mediated cyclization. If olefin is tethered with a nucleophilic center, intramolecular cyclization will occur. In contrast, when a substrate without a nucleophilic site was used, iodohydrin adducts were provided *via* the intermolecular nucleophilic attack of water onto the iodonium ions.

Shakhmaev and co-workers [35] have developed an efficient protocol for the synthesis of ethyl 5-phenylpent-2-en-4-ynoate by olefination-dehydrohalogenation of 2-iodo-3-phenylprop-2-enal obtained by the reaction between cinnamaldehyde and molecular iodine in the presence of 4-(dimethylamino)pyridine (DMAP) as the catalyst.

Meng and co-workers [36] have discovered a convenient and efficient method for iodination of arylacetylenes using I$_2$ and DMAP (4-dimethylaminopyridine) (Scheme 27) and the iodination of aryl acetylenic ketones by employing K$_2$CO$_3$ as a base providing the corresponding products in good to excellent yields (Scheme 28).
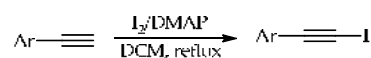
Scheme 27. Iodination of terminal acetylenes with I$_2$/DMAP.
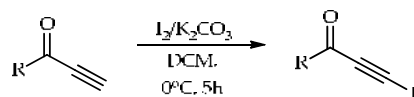
Scheme 28. Iodination of acetylene ketones with I$_2$/K$_2$CO$_3$.

Tsai and co-workers [37] have established a simple and environmentally friendly method for iodination of terminal alkynes catalyzed by CuI/TBAB (tetrabutylammonium bromide) under air in water providing the corresponding products in good to high yields (Scheme 29).

The efficient method for iodoarylation of arylalkynes with I$_2$ and PhI(OCOPh)$_2$ was developed [38], providing the corresponding products in moderate to good yields (Scheme 30).
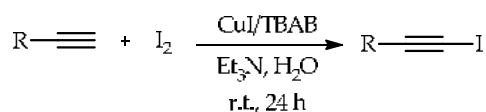
Scheme 29. Iodination of terminal alkynes catalyzed by CuI/TBAB.
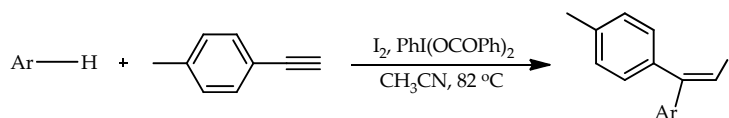
Scheme 30. Iodoarylation of arylalkynes with I_2 and PhI(OCOPh)$_2$.

Reddy and co-workers [39] developed an efficient protocol for oxy-iodination of alkynes using potassium iodide (KI) and *tert*-butyl hydroperoxide (TBHP), in the presence of methanol as a solvent, at room temperature affording the corresponding products in moderate to quantitative yields (Scheme 31).

Selected products:
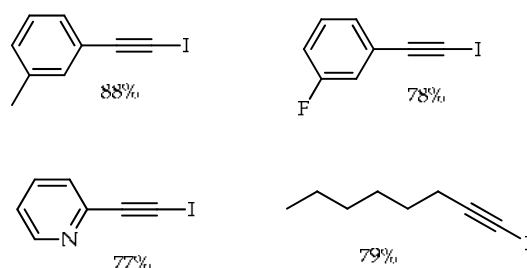
Scheme 31. Synthesis of 1-iodoalkynes employing KI/TBHP.

A novel and convenient protocol for the hydroiodination of alkynes has been established by Ogawa and Kawaguchi [40], employing I_2/hydrophosphine binary system affording the corresponding Markovnikov-type adducts in good yield. It was reported that this method could be a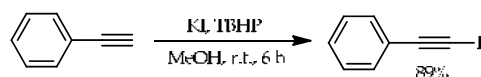pplied for iodinations of OH and COOH groups. Chobanyan and co-workers have reported the method for the synthesis of hydroalumantion-iodination of alkyne-1,4-diols [41].

Guo and co-workers [42] have reported a new approach for the synthesis of (E)-diiodoalkenes using alkyne as the starting material, ammonium persulfate as an oxidant, iodide as iodine source, and water as the green solvent, providing the corresponding products in good to quantitative yields (Scheme 32).
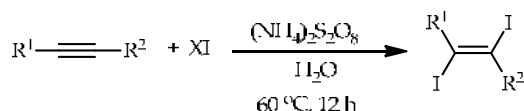
R^1, R^2: alkyl, aryl, carbonyl, ester
X = Na, K, NH$_4$

Scheme 32. Diiodination of alkynes with iodide in water mediated by (NH$_4$)$_2$S$_2$O$_8$.

It is assumed that oxidation of the iodide ion by the persulfate ion generates I_2, which further undergoes electrophilic *anti*-addition into the alkyne to afford the corresponding (*E*)-1,2-diiodoalkene (Scheme 33).

$$S_2O_8{}^{2-} + 2I^- \longrightarrow I_2 + 2SO_4{}^{2-}$$

$$R^1 \!\!=\!\! R^2 \;+\; I_2 \longrightarrow \begin{array}{c} I \quad R^2 \\ \diagup\!\!\!\diagdown \\ R^1 \quad I \end{array}$$

Scheme 33. Plausible reaction mechanism.

A convenient protocol for the iodination of *N*-propargyltriflamide between trifluoromethanesulfonamide and trifluoro-*N*-(prop-2-yn-1-yl)methanesulfonamide in the system *t*-BuOCl–NaI provided N-[(2E)-2,3-diiodoprop-2-en-1-yl]trifluoromethanesulfonamide has been described by Shainyan 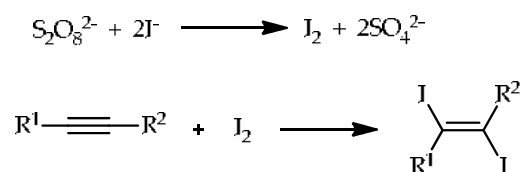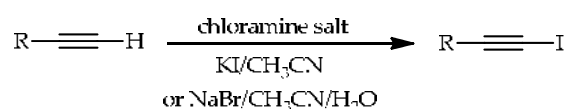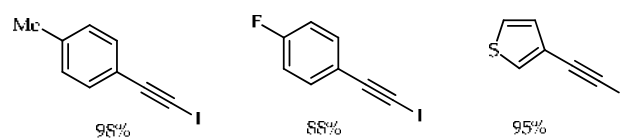and co-workers [43]. Oxidative halogenation of terminal alkynes has been reported by Lui and co-workers [44] mediated by chloroamine salt as the oxidant and KI as the halogen source providing 1-iodooalkynes in good to quantitative yields (Scheme 34).

$$R\!\!=\!\!H \xrightarrow[\substack{KI/CH_3CN \\ \text{or } NaBr/CH_3CN/H_2O}]{\text{chloramine salt}} R\!\!=\!\!I$$

Selected products:

98%   88%   95%

Scheme 34. Synthesis of 1-iodoalkynes mediated by chloramine salt.

Inexpensive and non-toxic reagents NH_4I (iodide source) and oxone (oxidant) were used for stereospecific oxidative (*E*)-diiodination of various alkynes such as aliphatic, aromatic, and heteroaromatic alkynes at room temperature in the presence of water as a green solvent [45] (Scheme 35).

up to 98% yield
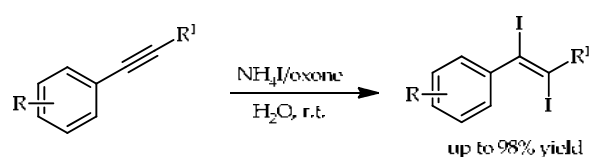
Scheme 35. Oxidative (*E*)-diiodination of alkynes using NH_4I/oxone system.

It is reported that oxone oxidizes the I^- (NH_4I) to form I^+ (HOI). This reactive species may react with alkyne to give a transient cyclic iodonium species, which further undergoes nucleophilic attack by I^- in situ from the opposite side of the cyclic iodonium ion to provide trans-diiodo alkene.

Ferris and co-workers have reported an efficient method for the iodination of terminal alkynes [46], employing a stoichiometric amount of KI and $CuSO_4$ in a mix of MeCN and sodium acetate buffer solution (pH 5).

Bathophenanthrolinedisulfonic acid (BPDS) was used to solubilize copper species in the solution (Scheme 36).
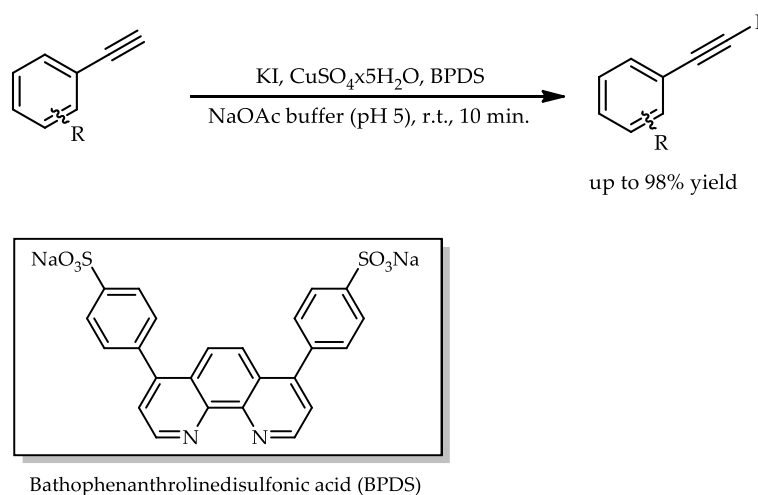
Scheme 36. Iodination of terminal alkynes mediated by KI/CuSO$_4$.

Han and Xiao [47] have developed an efficient and simple procedure for double-iodination of terminal alkynes using I$_2$ in the presence of water as the green solvent at room temperature. Moreover, by employing I$_2$/H$_3$PO$_3$ system, the selective hydroiodination of different alkenes and alkynes were obtained in good yields (Scheme 37).
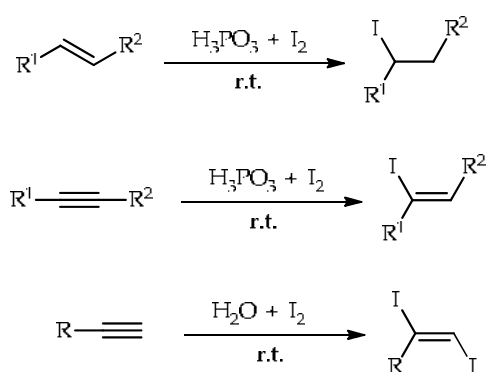
Selected products:
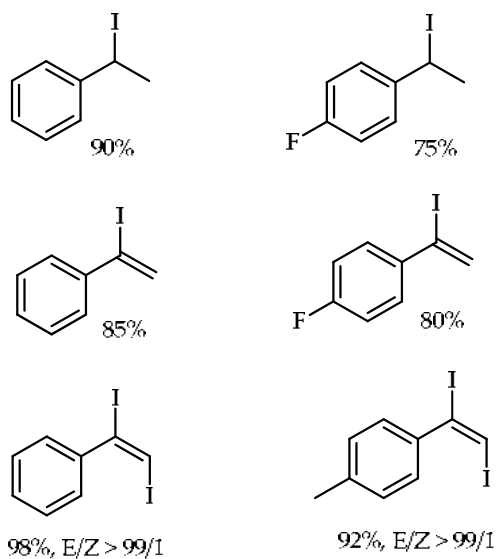
Scheme 37. Hydriodination and double-iodination of alkenes and alkynes using I$_2$.

Regarding the mechanism, it was reported that H_3PO_3 could react with molecular iodine to give hydrogen iodide HI, and then following the Markovnikov rule, provides the corresponding hydroiodination. For the double-iodination, I_2 undergoes electronic *anti*-addition to alkynes via a cyclic iodonium to provide the corresponding diiodoalkene (Scheme 38).
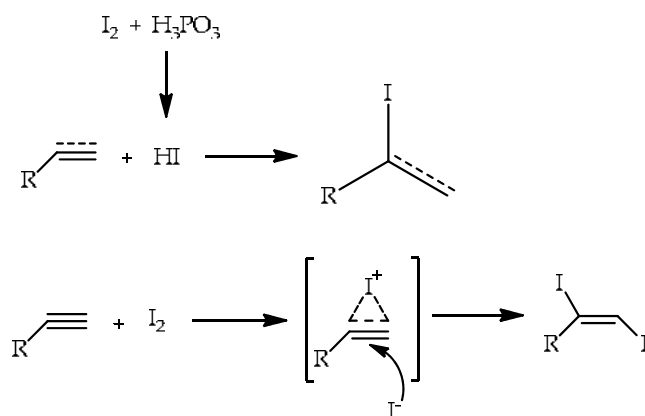
Scheme 38. Possible reaction pathway.

In 2020, Ghosh and co-workers [48] reported a metal- and oxidant-free method for synthesizing 1,1,2-triiodostyrenes by decarboxylative iodination of propiolic acids using I_2/NaOAc providing the corresponding products in good yields (Scheme 39). Moreover, β,β-diarylacrylic acids undergo decarboxylative mono-iodination under the same reaction conditions, affording 1,1-diaryl-2-iodoalkenes.

Selected products:
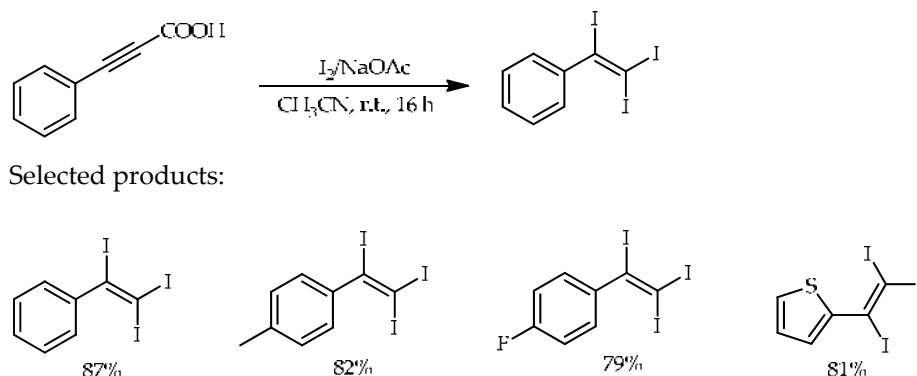
Scheme 39. Synthesis of 1,1,2-triiodostyrenes mediated by I_2/NaOAc.

In the same year, Lingling and co-workers [49] have published a convenient protocol for diiodination of alkynes employing sodium iodide (as iodine source) and air (as an oxidant) under the visible light, providing the corresponding products in moderate to high yields (Scheme 40).
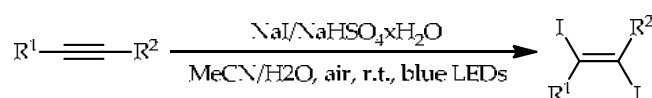
Scheme 40. Diiodination of alkynes mediated by NaI under the visible light.

Recently, an environmentally benign method for the aerobic oxidative iodination of terminal alkynes mediated by sodium sulfinate/KI was presented by Zhuo and co-workers [50] using ethanol as the green solvent at room temperature. Moreover, the

synthesis of symmetrical 1,3-diynes was presented via the iodination/homocoupling of terminal alkynes (Scheme 41).

Selected products:

81%   90%   87%
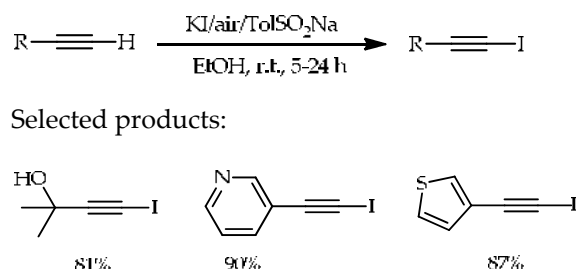
Scheme 41. Synthesis of 1-iodoalkynes mediated by TolSO$_2$Na/KI.

4. Iodination of Alkyl Carbonyls Compounds to α-Iodo Alkyl Carbonyl Derivatives

In 2008, Stavber and co-workers [11] had established an environmentally friendly methodology for aerobic oxidative α-iodination of carbonyl compounds using potassium iodide as iodine source catalyzed by sodium nitrite in acidic media providing the corresponding products in good to quantitative yields. In the case of aryl methyl ketones using MeCN as the solvent, iodination on the aromatic ring was occurred, while in the presence of aqueous EtOH as the solvent, the methyl group was iodinated (Scheme 42).

R = *p*-OCH$_3$ (84%)
R = *o*-OCH$_3$ (89%)
R = *p*-Cl (90%)
R = *m*-Cl (68%)
R = *m*-NO$_2$ (65%)

Scheme 42. Iodination of aryl alkyl ketones mediated by KI/NaNO$_2$/H$_2$SO$_4$ in aqueous EtOH.

Pavlinac and co-workers [51] have described an efficient methodology for the iodination of dimethoxy- and trimethoxy benzenes, aryl alkyl ketones and cyclic ketones by employing I$_2$/UHP (urea-H$_2$O$_2$) or I$_2$/30% aq. H$_2$O$_2$ in the water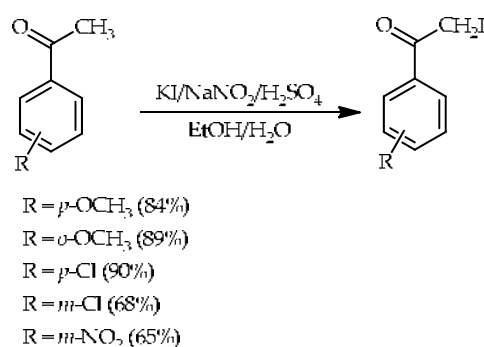 miscible ionic liquid (IL) 1-butyl-3-methyl imidazolium tetrafluoroborate (bmimBF$_4$) or in water immiscible IL, 1-butyl-3-methyl imidazolium hexafluorophosphate(bmimPF$_6$), providing the corresponding products in excellent yields. In terms of efficiency, 30% aq. H$_2$O$_2$ was superior to UHP as the mediator of iodination in both ILs for iodine introduction at methoxy substituted benzenes and alkyl site next to a carbonyl group (Scheme 43).
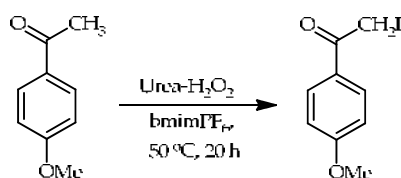
Scheme 43. Iodination of aryl alkyl ketones mediated by bmimPF$_6$/Urea-H$_2$O$_2$.

The same group of authors have developed [52] the green methodology for iodination of aryl methoxy substituted 1-indanone, 1-tetralone, and acetophenone using I$_2$/30% aq.

H_2O_2 as oxidant under solvent- and catalyst-free reaction conditions (SFRC). In the case of dimethoxy- and trimethoxy benzenes, iodination on the aromatic ring has occurred, while in the case of aryl alkyl ketones, iodination took place at the alkyl position next to a carbonyl group (Scheme 44).
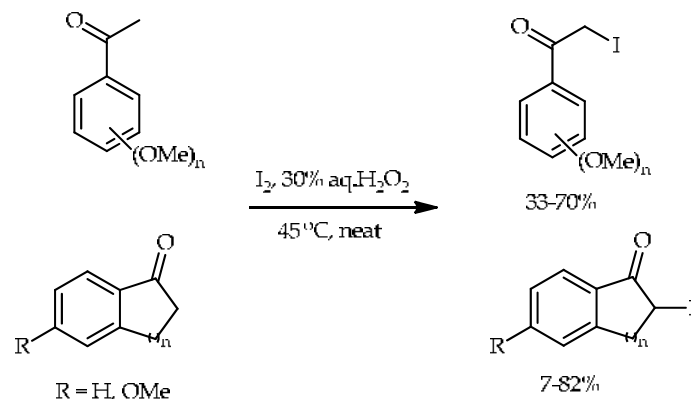
Scheme 44. Iodination of aryl alkyl ketones and cyclic ketones in the presence of I_2/30% aq. H_2O_2 under SFRC.

Furthermore, Iskra and co-workers [53] have reported an efficient, selective, and metal-free protocol for the iodination of aldehydes, alkyl ketones, and aromatics using I_2/$NaNO_2$/air/silica-supported H_2SO_4 in MeCN at room temperature. Air was used as the oxidant for the regeneration of I_2 from eluted HI with 100% iodine atom economy (Scheme 45).

R^1 = Bu, R^2 = Pr, (85%)
R^1 = Ph, R^2 = H, (91%)
R^1 = Ph, R^2 = CO_2Et, (94%)
R^1 = 1-tetralone, (91%)
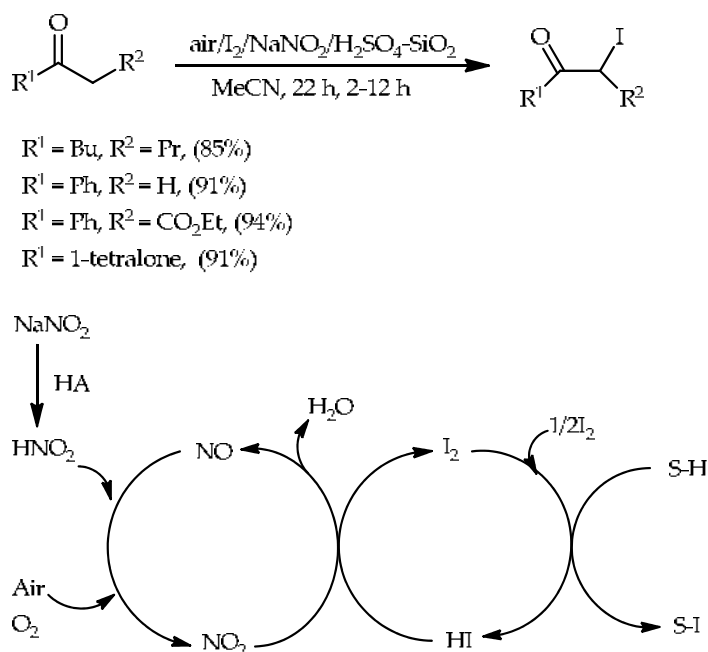
Scheme 45. Aerobic iodination of alkyl carbonyls using air/I_2/$NaNO_2$/acid system.

Yadav and co-workers [54] have reported a new and efficient method for the synthesis of α-iodo ketones and α-iodo dimethyl ketals in good to high yields, starting from acetophenones in the presence of I_2 and TMOF (trimethylorthoformate), (Scheme 46).
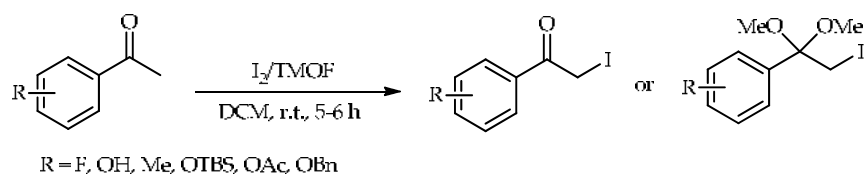
Scheme 46. α-iodination of ketones and dimethyl ketals with I_2/TMOF.

A convenient method for iodination of α,β-unsaturated ketones using copper (II) oxide/iodine in the presence of *i*-PrOH as the solvent has been reported by Wang and co-workers [55], providing the corresponding products in good to high yields (Scheme 47).
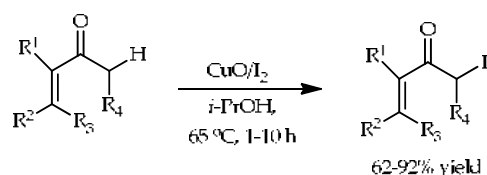
Scheme 47. Iodination of α,β-unsaturated ketones using CuO/I_2.

Terent'ev and co-workers [56] have reported the convenient method for synthesizing 2-iodo-1-methoxy hydroperoxides and their deperoxidation and demethoxylation to 2-iodo ketones. The reactions have occurred between enol ethers and the I_2-H_2O_2 system, providing the corresponding products in moderate to quantitative yields.

Stavber and co-workers [3] have established a novel and green methodology for iodination of ketones in an aqueous micellar system, in the presence of I_2, as the iodine source, air (terminal oxidant), $NaNO_2$ (catalyst), and H_2SO_4 (activator). The use of the aqueous solution of anionic amphiphile SDS (sodium dodecyl sulfate) was observed to be an excellent promoter than the use of water alone, improving the efficiency of the reactions (Scheme 48).
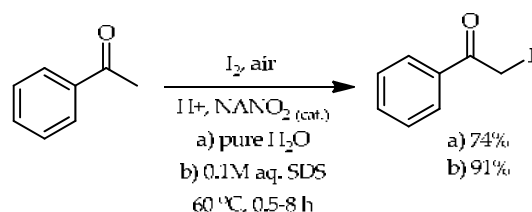
Selected products:
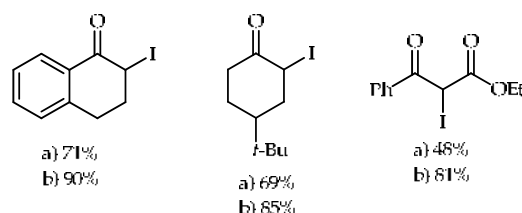
Scheme 48. Aerobic oxidative iodination of ketones.

Lee and co-workers have developed an efficient method for iodination of aryl alkyl ketones using I_2/HTIB [hydroxyl(tosyloxy)iodo]benzene or MeI/HTIB in [bmim]BF_4 ionic liquid, providing the corresponding products in good to excellent yields [57].

An efficient protocol for the synthesis of α-iodo ketones by oxidative iodination of ketones in the presence of iodine and *m*-iodosylbenzoic acid as a recyclable oxidant has been presented. The corresponding iodinated products are separated from side products

by treatment with anionic exchange resin Amberlite IRA 900 HCO_3^-, *m*-iodosylbenzoic acid can be recovered from Amberlite resin by treatment with HCl [58].

A convenient and selective synthetic protocol for iodination of 1,3-dicarbonyl derivative substrates has been reported by Khan and Ali [59] using vanadyl acetylacetonate, hydrogen peroxide, and sodium iodide at ice-bath temperature, providing the iodinated products in good yields (Scheme 49).
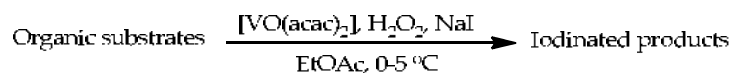
Selected products:
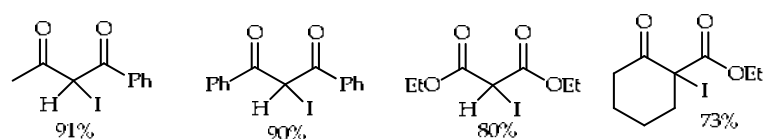
Scheme 49. Iodination of 1,3-dicarbonyls using $[VO(acac)_2]/H_2O_2/NaI$.

Moriya and co-workers [60] have reported a convenient method for reductive iodination of carboxylic acids to alkyl iodides using 1,1,3,3-tetramethyldisiloxane (TMDS) and I_2 catalyzed by $InBr_3$ in the presence of $CHCl_3$ as the solvent.

Prebil and co-workers [61] have developed air/$NH_4NO_{3(cat.)}/I_2/H_2SO_{4(cat.)}$ reaction system in the presence of MeCN as the solvent, for the α-iodination of aryl, heteroaryl, alkyl, and cycloalkyl methyl ketones. In the case of strongly activated aryl methyl ketones iodination took place regioselectively on the aromatic ring, (Scheme 50).

Selected products:

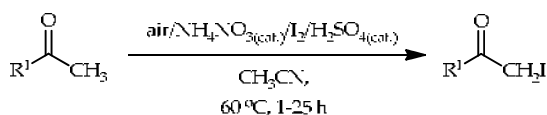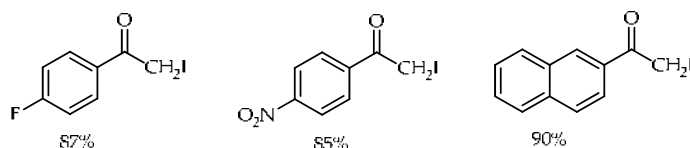**Scheme 50.** Aerobic oxidative α-iodination of alkyl methyl ketones using air/ $NH_4NO_{3(cat.)}/I_2/$ $H_2SO_{4(cat.)}$ reaction system.

Regarding the mechanism, in cycle I, iodination enol form of the ketone at α-position using I_2 has occurred, and I_2 has been reduced to HI. The re-oxidation of iodide to I_2 by NO_2 has been presented as cycle II. NO_2 has been reduced to NO when it completes the oxidation of iodide, while the oxidation of NO to NO_2 is accomplished with aerial oxygen. Acidic conditions have two leading roles: the first is to transform NH_4NO_3 to HNO_3, which is thermally supported decomposing equilibrium with NO_2, and the second is in tuning the reactivity by increasing enolization of the ketone (Scheme 51).

In 2014, Terent'ev and co-workers [62] reported mono-and bicyclic enol ethers reactions with I_2/H_2O_2, I_2–Bu^{t}OOH, and I_2–tetrahydropyranyl hydroperoxide combinations. The authors have presented that the reaction pathway depends on the nature of peroxide and the ring size. The reaction between 2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran with the I_2–hydroperoxide system provides iodoperoxides, α-iodolactones, and α-iodohemiacetals. Bicyclic enol ethers were converted into vicinal iodoperoxides only in the reaction with the I_2–H_2O_2 system (Scheme 52), while I_2–Bu^{t}OOH provides the hydroperoxidation product.

$$NH_4NO_3 + H_2SO_4 \rightleftharpoons HNO_3 + (NH_4)_2SO_4 \quad (1)$$

$$4HNO_3 \rightleftharpoons 4NO_2 + 2H_2O + O_2 \quad (2)$$
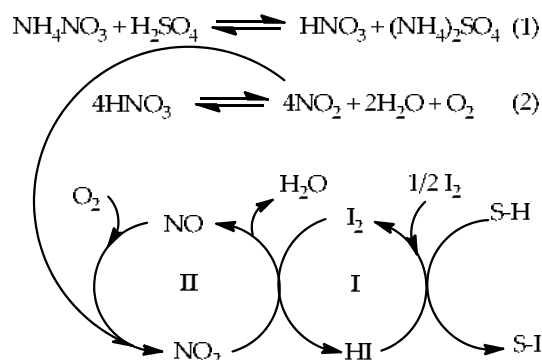
Scheme 51. The reaction pathway for the aerobic oxidative α-iodination employing air/ $NH_4NO_{3(cat.)}$/ I_2/$H_2SO_{4(cat.)}$.
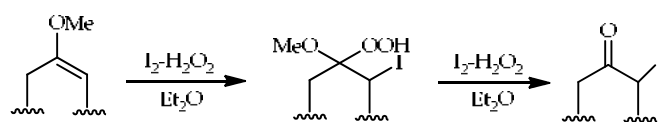
Scheme 52. Synthesis of 2-iodo-1-methoxyhydroperoxides and 2-iodo ketones using I_2–H_2O_2 system.

In 2011, Marri and co-workers [63] had reported a simple and efficient methodology for the α-monoiodination of carbonyl compounds employing NH_4I and oxone in methanol, providing the corresponding products in moderate to excellent yields (Scheme 53).

R = aryl, alkyl
R^1 = alkyl, aryl, H
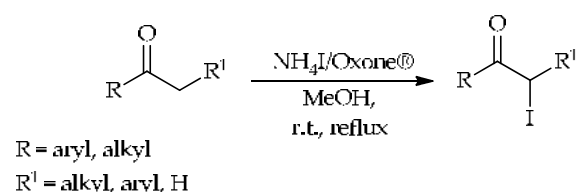
Scheme 53. α-Iodination of alkyl ketones using NH_4I/oxone® system.

It is reported that Oxone® oxidizes the I^- (NH_4I) to I^+ (HOI) which reacts with enol form of carbonyl compound to provide the corresponding α-iodo product (Scheme 54).

$$HSO_5^- + I^- \longrightarrow HOI^+ + SO_4^{2-}$$
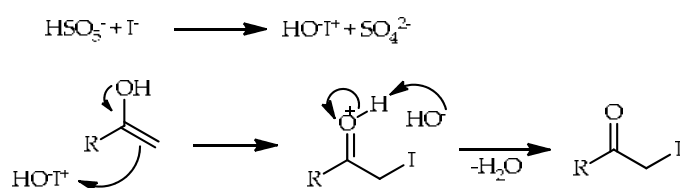
Scheme 54. Proposed reaction mechanism.

In 2015, Reddy and co-workers [64] had established a convenient and environmentally friendly protocol for the synthesis of α-iodo alkyl ketones starting from secondary alcohols, including benzylic and aliphatic alcohols (cyclic and acyclic) using ammonium iodide and oxone in aqueous media (Scheme 55).

Zhu and co-workers have reported the convenient method for the β-C (sp^3)-H iodination of ketones in the presence of palladium (II) as the catalyst employing aminooxyacetic acid auxiliary [65]. Sanz-Marco and co-workers [66] have developed an efficient and one-pot methodology for the synthesis of α-iodo alkyl ketones (as single constitutional isomers) starting from allylic alcohols and elemental iodine in combination with $NaNO_2$ as an oxidation catalyst and oxygen as the terminal oxidant. The protocol combines a 1,3-hydrogen shift mediated by Ir(III) complex (Scheme 56).
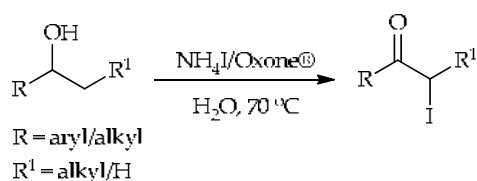
Selected products:
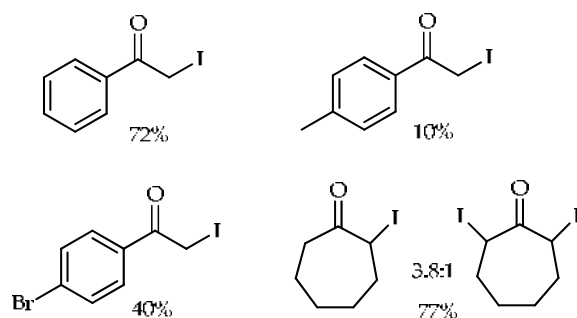
Scheme 55. Synthesis of α-iodo alkyl ketones using NH₄I/oxone® system.

$R^1 = H$, alkyl, aryl;
$R^2 = H$, alkyl, aryl
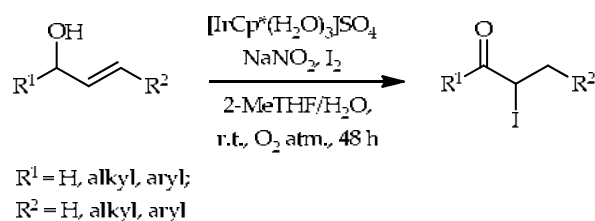
Selected products:
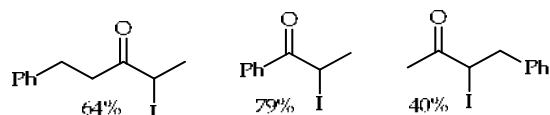
Scheme 56. Synthesis of α-iodoketones through aerobic oxidative iodination.

5. Conclusions

In summary, this review presents the progress of various methods for the iodination of organic compounds, including alkanes, alkenes, alkynes and alkyl carbonyls using elemental iodine or iodides. Aerobic oxidative and non-metal iodination strategies are also established. It should be emphasized that convenient methods have been developed in this field. Still, investigating and developing environmentally friendlier protocols in aqueous reaction media or under solvent-free can be considered an exciting research subject.

References

1. Togo, H.; Iida, S. Synthetic Use of Molecular Iodine for Organic Synthesis. *Synlett* **2006**, *2006*, 2159–2175. [CrossRef]
2. Küpper, F.C.; Feiters, M.C.; Olofsson, B.; Kaiho, T.; Yanagida, S.; Zimmermann, M.B.; Carpenter, L.J.; Luther, G.W., III; Lu, Z.; Jonsson, M.; et al. Commemorating Two Centuries of Iodine Research: An Interdisciplinary Overview of Current Research. *Angew. Chem. Int. Ed.* **2011**, *50*, 11598–11620. [CrossRef] [PubMed]
3. Stavber, G.; Iskra, J.; Zupan, M.; Stavber, S. Aerobic oxidative iodination of ketones catalysed by sodium nitrite "on water" or in a micelle-based aqueous system. *Green Chem.* **2009**, *11*, 1262–1267. [CrossRef]
4. Vekariya, R.H.; Balar, C.R.; Sharma, V.S.; Prajapati, N.P.; Vekariya, M.K.; Sharma, A.S. Preparation of α-Iodocarbonyl Compounds: An Overall Development. *ChemistrySelect* **2018**, *3*, 9189–9203. [CrossRef]
5. Mphahlele, M.J. Molecular Iodine-Mediated α-Iodination of Carbonyl Compounds. *J. Chem. Res.* **2010**, *34*, 121–126. [CrossRef]
6. Stavber, S.; Jereb, M.; Zupan, M. Electrophilic Iodination of Organic Compounds Using Elemental Iodine or Iodides. *Synthesis* **2008**, *2008*, 1487–1513. [CrossRef]
7. Chouthaiwale, P.V.; Suryavanshi, G.; Sudalai, A. NaIO$_4$–KI–NaN$_3$ as a new reagent system for C–H functionalization in hydrocarbons. *Tetrahedron Lett.* **2008**, *49*, 6401–6403. [CrossRef]
8. Giri, R.; Lan, Y.; Liu, P.; Houk, K.N.; Yu, J.-Q. Understanding Reactivity and Stereoselectivity in Palladium-Catalyzed Diastereoselective sp3 C–H Bond Activation: Intermediate Characterization and Computational Studies. *J. Am. Chem. Soc.* **2012**, *134*, 14118–14126. [CrossRef]
9. Zhu, R.-Y.; Saint-Denis, T.G.; Shao, Y.; He, J.; Sieber, J.D.; Senanayake, C.H.; Yu, J.-Q. Ligand-Enabled Pd(II)-Catalyzed Bromination and Iodination of C(sp3)–H Bonds. *J. Am. Chem. Soc.* **2017**, *139*, 5724–5727. [CrossRef] [PubMed]
10. Jereb, M.; Zupan, M.; Stavber, S. Hydrogen peroxide induced iodine transfer into alkenes. *Green Chem.* **2005**, *7*, 100–104. [CrossRef]
11. Stavber, G.; Iskra, J.; Zupan, M.; Stavber, S. Aerobic Oxidative Iodination of Organic Compounds with Iodide Catalyzed by Sodium Nitrite. *Adv. Synth. Catal.* **2008**, *350*, 2921–2929. [CrossRef]
12. Yang, Y.; Huang, X. Iodohydroxylation of Alkylidenecyclopropanes. An Efficient Synthesis of Iodocyclopropylmethanol and 3-Iodobut-3-en-1-ol Derivatives. *J. Org. Chem.* **2008**, *73*, 4702–4704. [CrossRef]
13. Yadav, J.S.; Subba Reddy, B.V.; Singh, A.P.; Basak, A.K. IBX/I2-mediated oxidation of alkenes and alkynes in water: A facile synthesis of α-iodoketones. *Tetrahedron Lett.* **2008**, *49*, 5880–5882. [CrossRef]
14. Yusubov, M.S.; Yusubova, R.Y.; Kirschning, A.; Park, J.Y.; Chi, K.-W. m-Iodosylbenzoic acid, a tagged hypervalent iodine reagent for the iodo-functionalization of alkenes and alkynes. *Tetrahedron Lett.* **2008**, *49*, 1506–1509. [CrossRef]
15. Yang, H.; Xu, B.; Hammond, G.B. Highly Regioselective Fluorination and Iodination of Alkynyl Enolates. *Org. Lett.* **2008**, *10*, 5589–5591. [CrossRef] [PubMed]
16. Sakee, U.; Nasuk, C.; Grigg, R. Synthesis of 1-C-(tetra-O-acetyl-β-d-galactopyranosyl)-2,3-diiodo-1-propene and its reaction with primary amines. *Carbohydr. Res.* **2009**, *344*, 2096–2099. [CrossRef]
17. Agrawal, M.K.; Adimurthy, S.; Ganguly, B.; Ghosh, P.K. Comparative study of the vicinal functionalization of olefins with 2:1 bromide/bromate and iodide/iodate reagents. *Tetrahedron* **2009**, *65*, 2791–2797. [CrossRef]
18. Nagura, H.; Kuribayashi, S.; Ishiguro, Y.; Inagi, S.; Fuchigami, T. Electrochemical iodofluorination of electron-deficient olefins. *Tetrahedron* **2010**, *66*, 183–186. [CrossRef]
19. Nobuta, T.; Hirashima, S.-I.; Tada, N.; Miura, T.; Itoh, A. Facile Aerobic Photo-Oxidative Synthesis of Phenacyl Iodides and Bromides from Styrenes Using I2 or Aqueous HBr. *Synlett* **2010**, *2010*, 2335–2339.
20. Chouthaiwale, P.V.; Karabal, P.U.; Suryavanshi, G.; Sudalai, A. Regiospecific Azidoiodination of Alkenes with Sodium Periodate, Potassium Iodide, and Sodium Azide: A High-Yield Synthesis of β-Iodoazides. *Synthesis* **2010**, *2010*, 3879–3882. [CrossRef]
21. Hanessian, S.; Focken, T.; Oza, R. Total Synthesis of Jerangolid A. *Org. Lett.* **2010**, *12*, 3172–3175. [CrossRef]
22. Samakkanad, N.; Katrun, P.; Techajaroonjit, T.; Hlekhlai, S.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. IBX/I2-Mediated Reaction of Sodium Arenesulfinates with Alkenes: Facile Synthesis of β-Keto Sulfones. *ChemInform* **2012**, *44*, 1693–1699. [CrossRef]
23. Kim, S.-H.; Kim, S.-H.; Lee, H.-J.; Kim, J.-N. One-Pot Synthesis of 5-Hydroxypyrrolin-2-one Derivatives from Modified Morita-Baylis-Hillman Adducts via a Consecutive CuI-Mediated Aerobic Oxidation, Allylic Iodination, Hydration of Nitrile, and Lactamization. *Bull. Korean Chem. Soc.* **2012**, *33*, 2079–2082. [CrossRef]
24. Yemets, S.V.; Shubina, T.E.; Krasutsky, P.A. Electrophilic monoiodination of terminal alkenes. *Org. Biomol. Chem.* **2013**, *11*, 2891–2897. [CrossRef] [PubMed]
25. Moskalik, M.Y.; Shainyan, B.A.; Astakhova, V.V.; Schilde, U. Oxidative addition of trifluoromethanesulfonamide to cycloalkadienes. *Tetrahedron* **2013**, *69*, 705–711. [CrossRef]
26. Gottam, H.; Vinod, T.K. Versatile and Iodine Atom-Economic Co-Iodination of Alkenes. *J. Org. Chem.* **2011**, *76*, 974–977. [CrossRef] [PubMed]
27. Wang, M.; Fu, C.; Ma, S. Highly Regio- and Stereoselective Iodohydroxylation of 1,2-Allenylic Sulfoxides in the Presence of Benzyl Thiol. *Adv. Synth. Catal.* **2011**, *353*, 1775–1786. [CrossRef]
28. Beltran, R.; Nocquet-Thibault, S.; Blanchard, F.; Dodd, R.H.; Cariou, K. PIFA-mediated ethoxyiodination of enamides with potassium iodide. *Org. Biomol. Chem.* **2016**, *14*, 8448–8451. [CrossRef] [PubMed]
29. Durgaiah, C.; Naresh, M.; Arun Kumar, M.; Swamy, P.; Reddy, M.M.; Srujana, K.; Narender, N. Regio- and stereoselective co-iodination of olefins using NH4I and Oxone. *Synth. Commun.* **2016**, *46*, 1133–1144. [CrossRef]

30. Kaswan, P.; Shelke, G.M.; Rao, V.K.; Kumar, A. Hydroxy-Group-Facilitated Vinylic Iodination of ortho-Vinylnaphthols Using Molecular Iodine. *Synlett* **2016**, *27*, 2553–2556.

31. Xinwei, L.; Song, S.; Ning, J. Oxidative Iodohydroxylation of Olefins with DMSO. *Acta Chim. Sinica* **2017**, *75*, 1202–1206.

32. Wang, H.; Chen, C.; Liu, W.; Zhu, Z. Difunctionalization of alkenes with iodine and tert-butyl hydroperoxide (TBHP) at room temperature for the synthesis of 1-(tert-butylperoxy)-2-iodoethanes. *Beilstein J. Org. Chem.* **2017**, *13*, 2023–2027. [CrossRef]

33. Hokamp, T.; Storm, A.T.; Yusubov, M.; Wirth, T. Iodine Monoacetate for Efficient Oxyiodinations of Alkenes and Alkynes. *Synlett* **2018**, *29*, 415–418.

34. Yi, W.; Wang, P.-F.; Lu, M.; Liu, Q.-Q.; Bai, X.; Chen, K.-D.; Zhang, J.-W.; Liu, G.-Q. Environmentally Friendly Protocol for the Oxidative Iodofunctionalization of Olefins in a Green Solvent. *ACS Sustain. Chem. Eng.* **2019**, *7*, 16777–16785. [CrossRef]

35. Shakhmaev, R.N.; Sunagatullina, A.S.; Ignatishina, M.G.; Yunusova, E.Y.; Zorin, V.V. Synthesis of Ethyl (2E)-5-Phenylpent-2-en-4-ynoate. *Russ. J. Org. Chem.* **2019**, *55*, 897–899. [CrossRef]

36. Meng, L.G.; Cai, P.J.; Guo, Q.X.; Xue, S. Direct Iodination of Monosubstituted Aryl Acetylenes and Acetylenic Ketones. *Synth. Commun.* **2008**, *38*, 225–231. [CrossRef]

37. Chen, S.-N.; Hung, T.-T.; Lin, T.-C.; Tsai, F.-Y. Reusable and Efficient CuI/TBAB-Catalyzed Iodination of Terminal Alkynes in Water under Air. *J. Chin. Chem. Soc.* **2009**, *56*, 1078–1081. [CrossRef]

38. Rahman, M.A.; Kitamura, T. Iodoarylation of Arylalkynes with Molecular Iodine in the Presence of Hypervalent Iodine Reagents. *Molecules* **2009**, *14*, 3132–3141. [CrossRef] [PubMed]

39. Rajender Reddy, K.; Venkateshwar, M.; Uma Maheswari, C.; Santhosh Kumar, P. Mild and efficient oxy-iodination of alkynes and phenols with potassium iodide and tert-butyl hydroperoxide. *Tetrahedron Lett.* **2010**, *51*, 2170–2173. [CrossRef]

40. Kawaguchi, S.-I.; Ogawa, A. Highly Selective Hydroiodation of Alkynes Using an Iodine−Hydrophosphine Binary System. *Org. Lett.* **2010**, *12*, 1893–1895. [CrossRef] [PubMed]

41. Gharibyan, H.A.; Makaryan, G.M.; Hovhannisyan, M.R.; Kinoyan, F.S.; Chobanyan, Z.A. Some special features of hydroalumination-iodination of alkyne-1,4-diols. *Russ. J. Gen. Chem.* **2014**, *84*, 457–464. [CrossRef]

42. Jiang, Q.; Wang, J.-Y.; Guo, C.-C. (NH4)2S2O8-Mediated Diiodination of Alkynes with Iodide in Water: Stereospecific Synthesis of (E)-Diiodoalkenes. *Synthesis* **2015**, *47*, 2081–2087. [CrossRef]

43. Astakhova, V.V.; Ushakov, I.A.; Shainyan, B.A. Oxidative iodination of N-propargyltriflamide. *Russ. J. Org. Chem.* **2017**, *53*, 953–954. [CrossRef]

44. Liu, X.; Chen, G.; Li, C.; Liu, P. Chloramine Salt Mediated Oxidative Halogenation of Terminal Alkynes with KI or NaBr: Practical Synthesis of 1-Bromoalkynes and 1-Iodoalkynes. *Synlett* **2018**, *29*, 2051–2055. [CrossRef]

45. Banothu, R.; Peraka, S.; Kodumuri, S.; Chevella, D.; Gajula, K.S.; Amrutham, V.; Yennamaneni, D.R.; Nama, N. An aqueous medium-controlled stereospecific oxidative iodination of alkynes: Efficient access to (E)-diiodoalkene derivatives. *New J. Chem.* **2018**, *42*, 17879–17883. [CrossRef]

46. Ferris, T.; Carroll, L.; Mease, R.C.; Spivey, A.C.; Aboagye, E.O. Iodination of terminal alkynes using KI/CuSO4–A facile method with potential for radio-iodination. *Tetrahedron Lett.* **2019**, *60*, 936–939. [CrossRef] [PubMed]

47. Xiao, J.; Han, L.-B. Ready access to organoiodides: Practical hydroiodination and double-iodination of carbon-carbon unsaturated bonds with I2. *Tetrahedron* **2019**, *75*, 3510–3515. [CrossRef]

48. Ghosh, S.; Ghosh, R.; Chattopadhyay, S.K. Oxidant- and additive-free simple synthesis of 1,1,2-triiodostyrenes by one-pot decaroboxylative iodination of propiolic acids. *Tetrahedron Lett.* **2020**, *61*, 152378. [CrossRef]

49. Lingling, L.; Yiming, L.; Xuefeng, J. Visible-Light-Promoted Diiodination of Alkynes Using Sodium Iodide. *Chinese J. Org. Chem.* **2020**, *40*, 3354–3361.

50. Zhou, P.; Feng, S.; Qiu, H.; Zhang, J. Sodiump-Toluenesulfinate/KI-Mediated Aerobic Oxidative Iodination of Terminal Alkynes for Synthesis of 1-Iodoalkynes and 1,3-Diynes. *Chinese J. Org. Chem.* **2021**, *41*, 394–399. [CrossRef]

51. Pavlinac, J.; Laali, K.K.; Zupan, M.; Stavber, S. Iodination of Organic Compounds with Elemental Iodine in the Presence of Hydrogen Peroxide in Ionic Liquid Media. *Aust. J. Chem.* **2008**, *61*, 946–955. [CrossRef]

52. Pavlinac, J.; Zupan, M.; Stavber, S. Iodination of Organic Compounds Using the Reagent System I2–30% aq. H₂O₂ under Organic Solvent-free Reaction Conditions. *Acta Chim. Slov.* **2008**, *55*, 841–849.

53. Iskra, J.; Stavber, S.; Zupan, M. Aerobic oxidative iodination of organic molecules activated by sodium nitrite. *Tetrahedron Lett.* **2008**, *49*, 893–895. [CrossRef]

54. Yadav, J.S.; Kondaji, G.; Shiva Ram Reddy, M.; Srihari, P. Facile synthesis of α-iodo carbonyl compounds and α-iodo dimethyl ketals using molecular iodine and trimethylorthoformate. *Tetrahedron Lett.* **2008**, *49*, 3810–3813. [CrossRef]

55. Wang, Z.; Yin, G.; Qin, J.; Gao, M.; Cao, L.; Wu, A. An Efficient Method for the Selective Iodination of α,β-Unsaturated Ketones. *Synthesis* **2008**, *2008*, 3675–3681.

56. Terent'ev, A.O.; Borisov, A.M.; Platonov, M.M.; Starikova, Z.A.; Chernyshev, V.V.; Nikishin, G.I. Reaction of Enol Ethers with the I2-H2O2 System: Synthesis of 2-Iodo-1-methoxy Hydroperoxides and Their Deperoxidation and Demethoxylation to 2-Iodo Ketones. *Synthesis* **2009**, *2009*, 4159–4166. [CrossRef]

57. Lee, J.-C.; Kim, J.-M.; Park, H.-J.; Kwag, B.-M.; Lee, S.-B. Direct Metal-free α-Iodination of Arylketones Induced by Iodine or Iodomethane with HTIB in Ionic Liquid. *Bull. Korean Chem. Soc.* **2010**, *31*, 1385–1386. [CrossRef]

58. Yusubov, M.S.; Yusubova, R.Y.; Funk, T.V.; Chi, K.-W.; Kirschning, A.; Zhdankin, V.V. m-Iodosylbenzoic Acid as a Convenient Recyclable Hypervalent Iodine Oxidant for the Synthesis of α-Iodo Ketones by Oxidative Iodination of Ketones. *Synthesis* **2010**, *2010*, 3681–3685. [CrossRef]

59. Khan, A.T.; Ali, S. A Useful and Convenient Synthetic Protocol for Iodination of Organic Substrates Using a Combination of Vanadyl Acetylacetonate, Hydrogen Peroxide, and Sodium Iodide. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 1239–1243. [CrossRef]

60. Moriya, T.; Yoneda, S.; Kawana, K.; Ikeda, R.; Konakahara, T.; Sakai, N. Indium(III)-Catalyzed Reductive Bromination and Iodination of Carboxylic Acids to Alkyl Bromides and Iodides: Scope, Mechanism, and One-Pot Transformation to Alkyl Halides and Amine Derivatives. *J. Org. Chem.* **2013**, *78*, 10642–10650. [CrossRef]

61. Prebil, R.; Stavber, S. Aerobic oxidative α-iodination of carbonyl compounds using molecular iodine activated by a nitrate-based catalytic system. *Tetrahedron Lett.* **2014**, *55*, 5643–5647. [CrossRef]

62. Terent'ev, A.O.; Zdvizhkov, A.T.; Kulakova, A.N.; Novikov, R.A.; Arzumanyan, A.V.; Nikishin, G.I. Reactions of mono- and bicyclic enol ethers with the I2–hydroperoxide system. *RSC Adv.* **2014**, *4*, 7579–7587. [CrossRef]

63. Marri, M.R.; Macharla, A.K.; Peraka, S.; Nama, N. Oxidative iodination of carbonyl compounds using ammonium iodide and oxone®. *Tetrahedron Lett.* **2011**, *52*, 6554–6559. [CrossRef]

64. Reddy, M.M.; Swamy, P.; Naresh, M.; Srujana, K.; Durgaiah, C.; Rao, T.V.; Narender, N. One-pot synthesis of α-iodoketones from alcohols using ammonium iodide and Oxone® in water. *RSC Adv.* **2015**, *5*, 12186–12190. [CrossRef]

65. Zhu, R.-Y.; Liu, L.-Y.; Yu, J.-Q. Highly Versatile β-C(sp3)–H Iodination of Ketones Using a Practical Auxiliary. *J. Am. Chem. Soc.* **2017**, *139*, 12394–12397. [CrossRef]

66. Sanz-Marco, A.; Možina, Š.; Martinez-Erro, S.; Iskra, J.; Martín-Matute, B. Synthesis of α-Iodoketones from Allylic Alcohols through Aerobic Oxidative Iodination. *Adv. Synth. Catal.* **2018**, *360*, 3884–3888. [CrossRef]