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Metal-free one-pot oxidative conversion: Molecular Iodine Mediated Oxidation Organic Reactions

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Abstract: Various oxidative compounds such as aldehyde, ketone ester, and acids can be produced in large yields by an effective iodine-mediated oxidative reaction of organic molecules. Molecular iodine is a generally available and commercially extremely inexpensive substance that induces oxidative esterification. With the comparison with different Brønsted acid catalysis, molecular iodine or iodophilic activations proceed the reaction onto a deoxygenation pathway. With only a few mol% of I_2, the oxidation occurs very quickly at room temperature. This approach could also be used to transport different benzil derivatives from nonactivated alkynes, such as diaryl acetylenes. Molecular iodine with several mild reagents such as aq. NH_3, ~30% aq. H_2O_2 and DMSO might be used to convert various one degree alcohols, particularly benzylic alcohols, into the corresponding aromatic amides in sufficiently high yields in a one-pot method. Similarly, by treating different benzylic chloride, bromide and iodide with a molecular iodine oxidation medium, the corresponding aromatic amides may be prepared in a one-pot method. The reactions in this section include transformation of several compounds into their respective oxidative products with the metal-free one-pot oxidative.

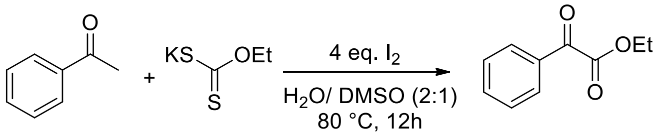
Introduction

Molecular iodine has long been employed in organic conversions due to its low cost & ease of handling. In recent year iodine-catalyzed reactions have been used for the synthesis of dehydration and condensation, glycosylation, conjugate addition and acetalization etc., replaced the early day oxidation process of metal catalysis. However, it's possible that a trace quantity of HI produced in situ acts as the real catalyst in some of these conversions. Lewis basic heteroatoms attack the molecular I_2 to form halogen bonding, which is produced by +ve polarization. The weak nature of such bonds, I_2 activation might be applied to carbon-carbon π-bonds in electrophilic metal catalysis and iodo-functionalizations of alkynes have actually afforded flexible synthetic approaches. However, catalytic alkyne activation in I_2 is unusually rare, owing to the production of extremely unfavorable reaction or nonspontaneous reaction I-Z (Z= Lewis base) bonds during catalyst turnover [e.g, bond dissociation energy (I-I) = 36 kcal/mol]. As part of these present report on the Brønsted acid-catalyzed oxidation of different precursor, can be replaced by molecular I_2-catalyzed alkynes activation.

Xianglin et al., (2020) recently stated that super-stoichiometric end oxidants viz., H_2O_2, TBHP, *m*-CPBA, chloramines, DMSO & hypochlorite have frequently been used in catalytic oxidation by iodous species. The oxidants hypoiodites (IO^-) and iodites (IO_2^-) were produce catalytically much active iodine species with the best oxidation states, similar to transition metal catalysis' inner-sphere oxidation. If the less reactive oxidants are used such dimethylsulphoxide or pyridine-N-oxides, the conversion needs to use the transition metal or Brønsted acid catalysis. The appointment of molecular iodine catalysis is poorly known, and radical explanations have been postulated for several the iodonium-mediated reactions.

Potassium xanthates with the many substituted groups, propyl, *n*-butyl, isopropyl, *n*-pentyl, isobutyl, and benzyl, were consistent with an iodine-mediated oxidative reac-

*Corresponding Author: swapaniict@gmail.com tion using a DMSO/H_2O solvent composition at 150°C to increase the yield of the reaction. Ethyl-2-oxo-2-phenylacetate can be synthesis in gram scale using the same method by the reaction of acetophenone with the theioether in an 83% yield.



Scheme 1. Ketones are used in the preparation of α – keto ester.

As reported by Iida et al., (2007), one of the most straightforward, less hazardous, and effective direct oxidation processes is the oxidation of primary alcohol to matching nitriles in molecular I_2/water, NH_3. In case, 3-alkyl alcohol was acted with molecular I_2/water, NH_3 gas under an empty balloon at a different temperature. One carbon less nitrile was produced. As a result of this reaction, we can produce propionitrile from n-butanol.

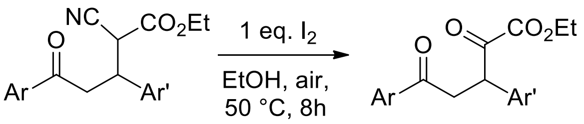
$$RCH_2OH \xrightarrow[\text{aq. } NH_3 \text{ (3.0mL), } 60\ °C]{I_2 \text{ (3.0 eq.)}} R\text{-}CN$$

Scheme 2. The oxidation of alcohol to nitriles using I_2/aq. NH_3 is demonstrated.

An autoclave or sealed tube was used to conduct the reaction, where the requirement of aq. NH_3 can be reduced. The reaction is particularly useful for large scale production in an autoclave, however, it is less useful for small scale production in a sealed tube. At 60°C, a total of 3.0 eq. of molecular I_2 and very much excess of aq NH_3 (28–30%) are required, yielding the highest yield 3-phenyl-propionitrile.

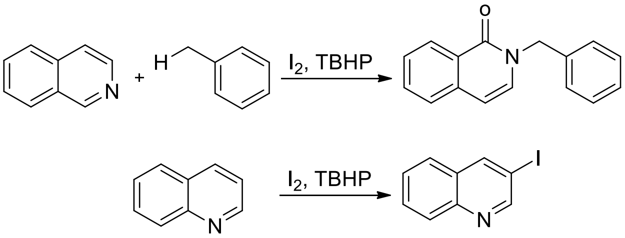
Researchers Xu et al., (2020) discovered an incomprehensible iodine-raised aerobic oxidation of cyano-keto esters. The reactions are very much facile to synthesize the cyano-keto esters. After substituting a Me-group for the phenyl ring of chalcone, 2-naphthyl, 2-furyl with one of the groups mentioned above using any of the solvent like DMF (N, N-dimethyl formamide) or MeCN (acetonitrile), it was discovered that the isolated products were yielded between 51–75%.

Interestingly, electron-donating groups like methyl and o-methyl or electron-withdrawing groups like nitro on the phenyl ring next to the carbon-carbon double bond in chalcones performed well in this reaction, yielding materials in the range of 73–87%. The 2, 4-dichloro-substituted chalcone demonstrated great reactivity as well, yielding α, δ-dicarbonyl ester in a good yield of 92% in the presence of acetic acid.



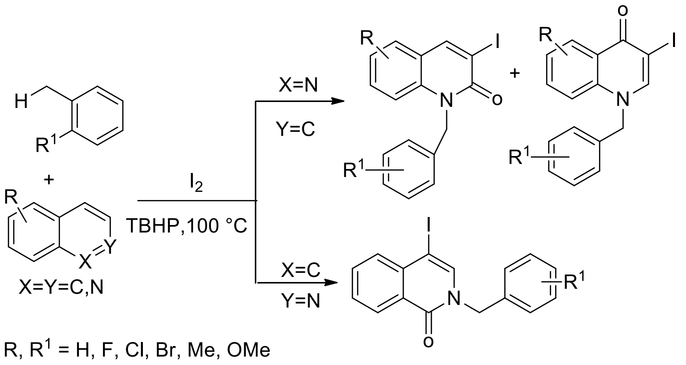
Scheme 3. The synthesis of α, δ-dicarbonyl esters is accomplished in two steps.

According to Luo et al., (2016) an effective oxidative coupling metal-free approach was developed to synthesize N-benzylidene-quinolin-1-(2H)one, C-H fictionalisation of azarenes with methylarenes the synthesis of N-benzylidene-quinolin-1-(2H)one, all in the appearences of catalytic amounts of molecular I_2. The first time this type of metal-free regioselective iodination of quinolines at the C_3 position by any molecular I_2 has been demonstrated in TBHP is noteworthy.



Scheme 4. The oxidative functionalization of isoquinoline is mediated by iodine/TBHP.

Molecular iodine is a commonly available chemical, simple to handle, and inexpensive on a commercial scale, and it has received a great deal of interest in recent decades. Aside from that, the combination of iodine and TBHP has been widely employed as an oxidant in various applications under extremely flexible settings to carry out various transformations.



Scheme 5. The synthesis of (iodo) isoquinolinones/quinolones is described here.

In particular, in recent years, numerous groups have been investigating the synthetic value of metal-free catalysts, primarily iodine and iodide salts, for a variety of func-

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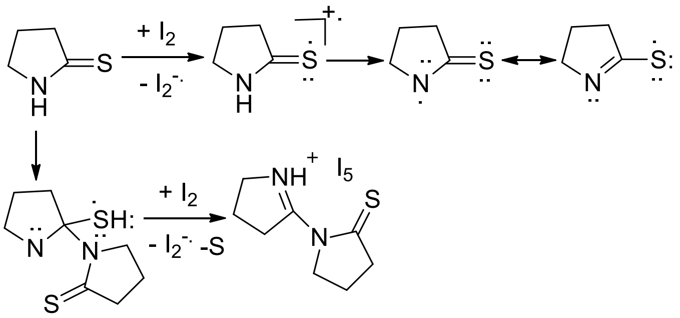
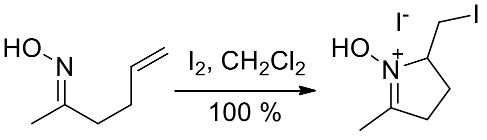
tionalizations, to improve their efficiency. A straight forward approach for preparing N-benzyliodo cast away quinolones & isoquinolines in a one-pot oxidative triple functionalization of the azaarenes and methylarenes by employing molecular I_2 and TBHP as an oxidant was described in this paper by Shantharjun et al., (2015).

Two thioamide molecules can form S-coordination by I^+ coming from the heterolysis of the diiodine in the presence of molecular iodine/iodonium salts. The iodonium salts' $Ar(R)I^+X$ (where R is the alkynyl, alkenyl, or fluoroalkyl group) structures and reactivity have been examined in detail in their review of Margarita et al., 2013. It was imagined that when joined with ionic iodide species (as I or I_3), and hypothesis that diiodine results in the formation of a vast range of oligomeric anionic polyiodides.



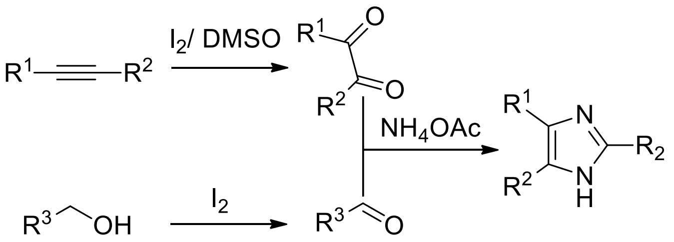
Scheme 6. Pyrrolidine-2-thione in the available of molecular iodine.

Using a new synthetic approach based on iodine-mediated oxidation of desulphurization in conjunction with the N-2-pyridyl methyl thioamides cyclization mechanism, 2-azaindolizanes may be synthesized for the first time. As a result of the interaction of N-2-pyridylmethyl-2-pyridine carbothioamide with molecular I_2, azaindolizine is yielded in 89% of cases, and the sulphur-bridged 2-azaindolizine dimer (7% yield) formed as well as an uncommon molecule, The tricyclic analogues of quinolone antibacterial drugs can be synthesized from the N-arylpyrrolodine-2-thiones as the precursors, which has resulted in the discovery of new antibacterial agents.



Scheme 7. N-arylpyrrolodine-2-thiones are made in the way.

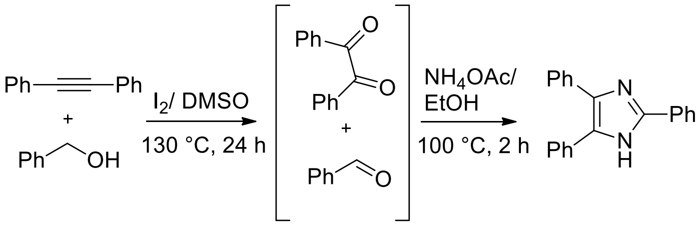
A range of trisubstituted imidazoles were converted, first from Internal alkynes to 1,2-diketones utilizing an I_2/DMSO oxidation system, which was then treated by the addition of various aldehydes and ammonium acetate.



Scheme 8. One-pot conversion to 2,4,5-trisubstituted imidazoles.

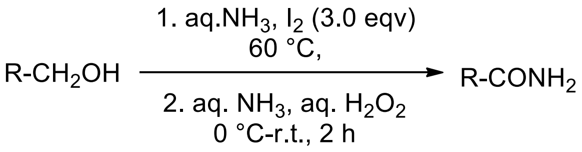
The reagent molecular iodine and DMSO mixture has shown to be a useful tool for synthetic organic chemists, with this system being reported to fulfill in two ways: The reactions catalyzed by I_2 in a DMSO medium, & I_2/DMSO treated oxidative transformations.

This powerful system can perform a wide range of transformations, including the oxidative cross-coupling of alkynes to glyoxals, for example the unsymmetrical synthesis of organochalcogenides, dehydrogenation, and the cleavage of oxidative cross-coupling from the selective sulphenylation of electron-rich arenes and carbonyl compounds. With this expertise, the possibility of iodine-mediated two fold oxidation of readily available starting materials (internal alkynes and primary alcohols) in the same reaction vessel piqued the attention of researchers, who hypothesised that this would contribute to their respective intermediates (diketones and aldehydes) that, in the presence of ammonium acetate, would eventually converge to the desired 2, 4, 5-trisubstituted imidazoles sparked their interest.



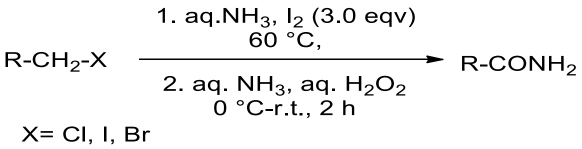
Scheme 9. Synthesis of 2,4,5- trisubstituted imidazoles.

The investigation of the one-pot oxidative conversion of benzylic alcohols to their respective amides is being done. For 2 hours at 60°C, a mixture of 4-methylbenzyl alcohol and molecular I_2 in aq. NH_3 (28–30%) was warmed. It was then necessary to cool the reaction mixture to 0°C before adding the acid NH_3 back in. Finally, using a dropping funnel, drop wise additions of 30 % aq. H_2O_2 were made to the reaction mixture. Following being agitated for 2 hours at room temperature, the mixture was placed in aqueous saturated Na_2SO_3 and then extracted with $CHCl_3$ to obtain 4-methylbenzamide in 91% yield, after which it was dried under vacuum.



Scheme 10. Preparation of 4-methylbenzamide with I_2, aq. NH_3.

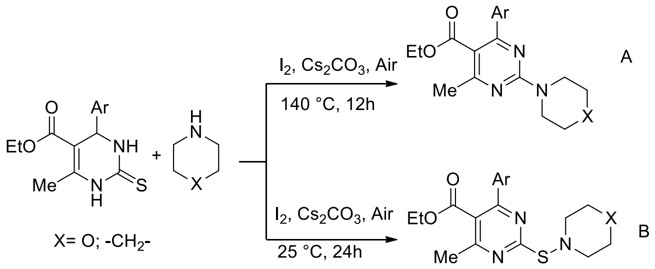
The following procedure investigated the oxidative one-pot conversion of benzylic halides to amides. Warming of a mixture of 4-methyl-benzyl chloride and molecular iodine in aq. NH_3 for 4 hours at 60°C was performed. The reaction composition was then cooled to 0°C, aq. NH_3 was assembled once more, and 30% aq. H_2O_2 was gently added using a dropping funnel. After completion of the reaction the reaction mixture was quenched with aq. saturated Na_2SO_3, and organic part was extracted with $CHCl_3$ to provide 4-methyl-benzamide in 81% yield after being agitated for 2 hours at room temperature. 4-methyl-benzyl bromide and 4-methyl-benzyl iodide were treated the same way and yielded good yields of 4-methyl-benzamide. Another possibility is that various iodides, benzylic bromides, or chloradies can be converted to corresponding amides in high yields. However, the identical treatment of alkyl halides resulted in low yields of the corresponding amides and the initial alkyl halides and amines.



Scheme 11. The oxidative transformation of benzylic halides into aromatic amides can be accomplished in a single pot.

The plausible mechanism for producing S–N and C–N coupling products based on these results and the stated approach, as indicated. Air and I_2 catalysed the synthesis of disulphide D, followed by S–N and C–N coupling of the starting material with morpholine at ambient temperature and 140°C, respectively. LC–MS revealed the production of the intermediate and A with B in the reaction of 3, 4-dihydropyrimidin-2-thiones with morpholine at 100°C. Another mechanism is also possible. That example, by replacing A with morpholine, the C–N coupling reaction can be completed. The C–N product B was formed from A with morpholine in PEG-400 at 140°C for 5 hours, which was validated by the reaction of A with morpholine in PEG-400. Iodine believes to be, functions as a catalyst and an oxidant simultaneously. In the appearance of oxygen from the air and Cs_2CO_3, it was believed iodine is likely converted into some hypervalent iodine species. This could explain why the reaction re-quires such a large amount of I_2.

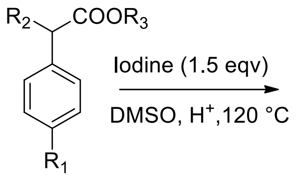
Using iodine as a catalyst, Vivek and colleagues (2014) report the oxidative de-alkoxycarbonylation of alternatively alkylphenyl acetates in which iodine is illustrated as a product in the process. The alkyl phenylacetate can be easily synthesized with the reaction of readily available phenyl acetic acid with alkyl halides and potassium carbonate in dimethylformamide, which was then evaporated.



Scheme 12. The coupling/aromatization of amine and 3,4-dihydropyrimidin-2-thiones.

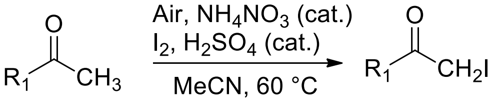
First, they chose Prop-2-en-1-yl phenylacetate as a model starting material for investigating the efficacy of dealkoxy-carbonylation by using a catalytic amount of molecular iodine in a catalytic amount of water. At room temperature, there was no discernible difference in the results. When the temperature of the reaction composition was raised to 80°C, only dealkylation could be detected, and no other reactions occurred. According to the findings, this type of result is consistent with our earlier results. After increasing the amount of iodine in the solution by one equivalent, the de-allyloxy-carbonylated product (48%) was obtained, along with the recovery of the unreacted starting material. However, increasing the temperature to 120°C resulted in the isolation of the oxidative product in 62%.

The methyl and ethyl phenyl acetates offered good yields, whereas the allyl and benzyl derivatives gave a modest yield. Several solvents were tested as reaction mediums, including dichloromethane, methanol, dimethylformamide, di-phenylether, and ethylene glycol. In the oxidative de-alkoxy-carbonylation procedure, DMSO was discovered to be an effective solvent and extend this process for numerous ethyl phenyl acetate derivatives to evaluate the generality of this new approach and the adaptability of the iodine mediated oxidative de-alkoxy-carbonylation. De-alkoxy-carbonylation of substrates with electron-withdrawing and donating groups yields a satisfying yield. However, despite several substrates producing a clean and smooth reaction, hydrolysis was preferred under ideal conditions.



Scheme 13. Direct oxidative de-ethoxycarbonylation by molecular iodine.

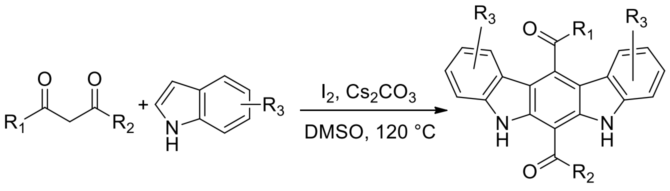
Under aerobic oxidative circumstances, Rok et al., (2014) developed the α-chlorination of aryl and alkyl methyl ketones with an effective and regioselective reaction system consisting of air/NH_4NO_3(cat.)/I_2(cat.)/HCl. A catalytic quantity of molecular I_2 was used to enable medium to quantitative and regioselective α-chlorination, with 2-iodo-1-(4-methoxyphenyl)ethanone as the major product and 2-chloro-1-(4-methoxyphenyl)ethanone as the side product, using a catalyst consisting of 50 mol% I_2 and HCl.



Scheme 14. Aerobic oxidative α-iodination of ketones.

The air/NH_4NO_3 (cat.)/I_2/H^+ oxidation condition for aerobic oxidative iodination of methyl ketones has been optimised in response to rising global demand for such iodomethyl ketone derivatives generated in direct single-step reactions under green condition.

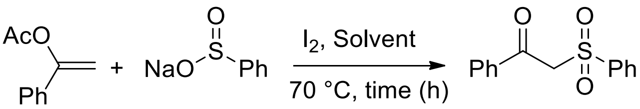
Ethyl benzoyl-acetate and 1H-indole were chosen as model substrates by Xue et al., (2015), to optimize reaction conditions in the presence of molecular iodine and base. The reaction was placed with 1.0 equivalent of I_2 and 0.25 equivalent of Cs_2CO_3 in DMSO at 80°C for 12 hours, yielding the product in 14% yield. The product could not be obtained when the dosage of Cs_2CO_3 was altered, neither up nor down. The reaction was then tested for various bases. On the other hand, the majority of the bases were passive. Cs_2CO_3, DIPEA, and NEt_3 could only aid the reaction.



Scheme 15. The formation of indolo[2,3-b]carbazole.

Following that, a variety of temperatures were tested in order to improve the yield, with 120°C being found to be the best temperature for the reaction. The percentage yields of the reaction were affected by the iodine dosage. When the dose of I_2 was reduced to 0.5 eq. 0.1 eq., no product was formed. When the dose of I_2 was raised to 1.5 eq., the product yield did not improve. When dry DMSO was utilized as a solvent, the yield could be raised to 50%. Finally, 1.5eq. ethyl benzoylacetate, 1eq. 1H in-dole, 1eq. iodine, and 0.25eq. Cs_2CO_3 in DMSO at 120°C for 12 hours were found to be optimum.

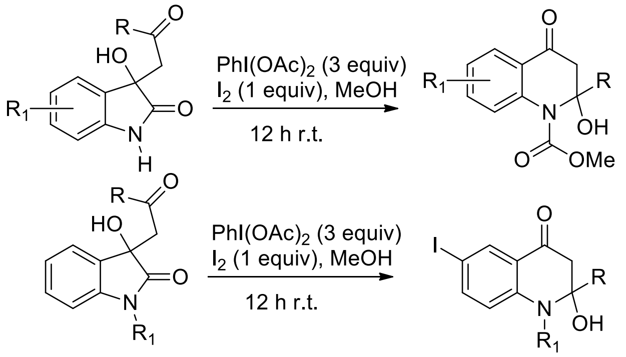
Employing aryl enol acetate as a substrate for the reaction, sodium sulphonate as a sulphonaylating agent, and I_2 as an oxidant, Yadav et al., (2016) reported the production of -keto sulphones. Most gratifyingly, in the presence of this metal-free oxidant, the required product was formed with a high yield. The reaction was carried out for 10 hours at ambient tempersture to achieve the required product but only 26% yield.



Scheme 16. The preparation of enol acetates for the preparation of keto sulphones.

Furthermore, the yield increased marginally when the reaction was carried out at 450°C. As a result, the reaction was repeated the process at various temperatures and discovered that the best yield (90%) was produced at 70°C. It was noted that the product could not have been created without the presence of an I_2. A decrease in the quantity of I_2 loaded from 1 mmol to 0.5 mmol resulted in a reduced yield of the product, whereas increasing the amount of I_2 from 1.5 mmol from 1 mmol did not affect the yield.

Certain additives can alter the oxidizing capacity of phenyliodine(III) diacetate (PIDA), as a result, the investigated the various combinations of phenyliodine(III) diacetate (PIDA) with molecular I_2 for oxidation, as previously described by the Kavale et. al., (2021) for oxidation. Using PIDA (1eq.) and I_2 (0.5eq.), it was discovered



Scheme 17. Oxidativesynthesis of 1-substituted-2-hydroxy-2-aryl/alkylquinolin-4(1H)-one.

that the oxidation of starting material to generate product occurred in a 16% yield when the two chemicals were combined. Increased reaction time, combined with excess equivalents of both PIDA and I_2, led to the product in

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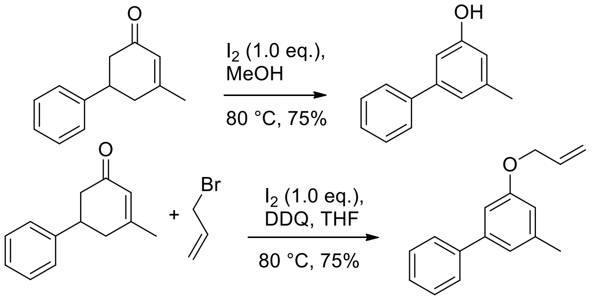
higher yields than previously reported. The optimal reaction conditions were achieved utilizing a 3:1 M equivalent ratio of PIDA and I_2 at room temperature, stirring for 12 hours, which resulted in the total removal of the starting material (TLC) and the synthesis of product in an 84% yield.

Jiang et al., (2021) reported one of the most efficient conversions of α,β-unsaturated cyclohexane to phenol using molecular I_2/DDQ, as an H-transferring oxidant for aromatization, it is one of the most extensively utilized compounds.

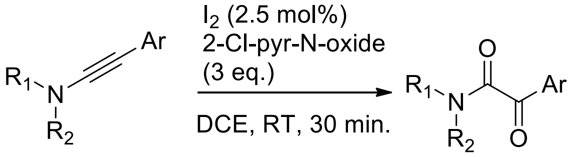


Scheme 18. α,β-unsaturated cyclohexane to phenol using molecular I_2/DDQ.

DDQ was used as the oxidant in this study, and the researchers hypothesized that meta-substituted alkoxybenzenes might be produced from the cyclohexenone skeleton in the same way. A model reaction was chosen for this purpose, and it was 3-methyl-5-phenyl-2-cyclohexenone, which could be easily synthesized from benzaldehyde and acetone using the Robinson annulation method, was used to investigate the viability of this oxidative aromatization.

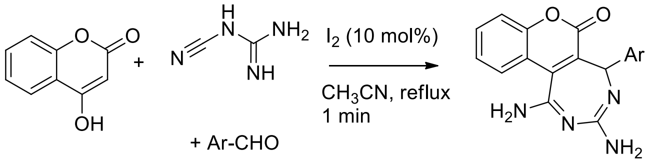
As a result, there was no reaction, which was depressed in nature. The molecular iodine catalysis in various reaction types and used molecular I_2 as the catalyst in this reaction, and the desired product was generated at a high yield. When the reaction was carried out in the presence of catalytic molecular iodine in the presence of several oxidants, it was discovered that neither H_2O_2 nor NBS could enhance the transformation, while Ag_2O was utterly ineffective in this synthesis.

In their paper, Kim et al., (2018) reported that the rapid oxidation of hydroiodic acid by 2-Cl-pyridine-N-oxide formed I_2, which then promoted the oxidation because as Kim group proved that treating 2-Cl-pyridine-N-oxide with 2eq. of hydroiodic acid promptly generated 2-Cl-pyridine, most likely in a reversible fashion. As a result, the formation is most likely the result of the action of I_2, rather than HI. This was confirmed by the fact that the redox-inactive Brønsted acid, $HNTf_2$, was unable to be produced. They were encouraged by the effectiveness of this N-oxide mediated oxidation of dynamites and decided to investigate the potential application of this iodine catalysis. A wide range of dynamites with different N-sulphonyl groups (mesyl, p-Toluenesulphonyl) performed exceptionally well under the given conditions. N-alkyl, allyl, benzyl and aryl groups were well accommodated, and the chemoselectivity was excellent for all of them. In general, Ar groups with abundant electrons oxidised sub-strates more quickly and selectively than Ar groups with few electrons. The presence of a stereochemically inhib-ited aryl group or a heteroaryl group had no detrimental effect. The reaction of a carbamate substrate, on the other hand, produced a poorer outcome, even when I_2 loading was increased to 40 mol%, and the temperature was raised to 80^0C. Unfortunately, even under tougher condi-tions, substituting the aromatic group with alkyl (n-hexyl), CO_2Et, or terminal dynamites did not result in a conversion of any kind.



Scheme 19. The oxidation of ynamides is catalysed by iodine.

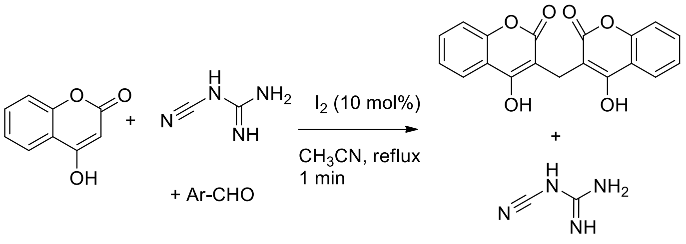
Using 4-hydroxycoumarin, cyanoguanidine, and benzaldehyde as starting materials in MeCN in the presence of catalytic amounts of I_2 (10 mol%), the Kidwai group (2007) synthesised 7-arylbenzopyrano [1,3]diazepines at room temperature. They were overjoyed when they discovered the development of benzopyrano[1,3]diazepines in 84% of the samples after 12 hours. The reaction did not produce any product in the absence of a catalyst, despite taking a lengthy period.



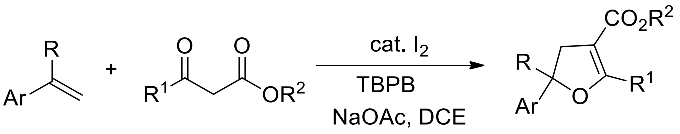
Scheme 20. The synthesis of 7-arylbenzopyrano [1,3]diazepines was catalysed by iodine.

With these standardized results in hand, further experiments were carried out to determine the optimal reaction parameters. Increases in the amount of iodine used, up to a maximum of 50 mol%, improve the yield of the final product. An increase in the reaction rate was also observed when the temperature was raised. Consequently, they proceed with 10 mol% molecular iodine under reflux circumstances to employ only the catalytic amount of iodine available.

Researchers Tang et al., (2015) discovered that using I_2 and tert-butyl peroxybenzoate (TBPB) in conjunction with NaOAc as an additive could produce favourable results when oxidative coupling/annulation of p-methylstyrene with methyl acetoacetate was carried out at low temperature and pressure. It was possible to generate the desired dihydrofuran with a high isolated yield (77%) and strong regioselectivity. As a result of the positive results obtained, the process then carried out with different functional group to check the tolerance level for synthesising various dihydrofurans under similar conditions.



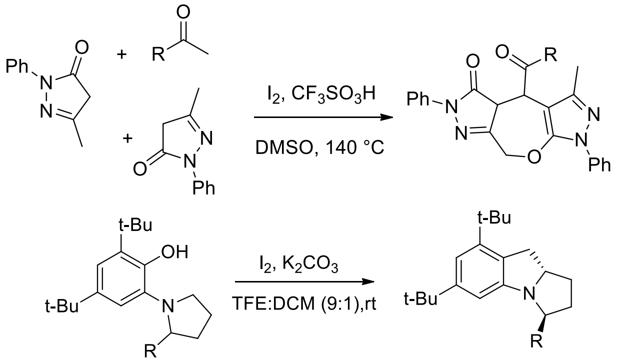
Scheme 21. In a protic solvent, the compound 3,3-phenylmethylenebis-(4-hydroxycoumarin) is synthesised.



Scheme 22. A study of the cross-coupling and annulation of β-Keto esters with alkenes was conducted.

The coupling product was obtained in 72% of the cases using para-tert-butylstyrene. This transition was made possible by the presence of electron-rich *p*-methoxystyrene. In this transformation, halide substituents were allowed, and the reaction provide the cyclization product, chemoselectively. Furthermore, containing a reactive chloromethyl group at the para position of the styrene could also be used to prepare the required product in a reasonable amount of time and yield.

Xu et al., (2020) investigated diverse reaction conditions for the iodine-catalyzed C-O bond formation process by testing many aryl methyl ketone substrates with various substitution patterns and functional groups, as reported in the journal Chemistry. It was found that a large no of functional groups could be tolerated and transformed, including methoxy, ethoxy, methyl, 3,5-nitro, cyano, carbomethoxyl, methyl-enedioxyl, chloro, and bromo substituents, as well as other functional groups. The related compounds were produced in moderate to good products with a variety of functional groups, and the results were analysed.



Scheme 23. Regioselective oxidation and formation of N,O-Acetals.

Conclusion

The metal free molecular iodine oxidation processes were widely used in last few decades. Here we covered few of the important reaction in this paper, enlight, late-stage techniques for the chemoselective oxidation of different functional group to provide the desired oxidative product under mild conditions. These approaches have the potential to be widely used in the different medicinal and pharmaceutical production process chemistry in a diverse range of materials from a small subset of molecular precursor, taking synthetic advantage to drug metabolites and potentially speeding up the hit-to-lead process of drug discovery scale up when contrasted to more conventional linear routes, which reduced the total costing of the final products.

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References

Iida, S., & Togo, H. (2007). Direct Oxidative Conversion of Alcohols and Amines to Nitriles with Molecular Iodine and DIH in aq. NH_3. *Tetrahedron*. 63: 8274–8281.

Jiang, D., Jia, X., Zhang, S., Zhang, Z., Li, L., & Qiao, Y. (2021). Iodine-Catalyzed Tandem Oxidative Aromatization for the Synthesis of meta-Substituted Alkoxybenzenes. *Tetrahedron*. 91: 132219.

Kavale, A. C., Kalbandhe, A. H., Opai, I. A., Jichkar, A. A., & Karade, N. N. (2021). Oxidative ring expansion of 3-hydroxy-3-phenacyloxindoles using phenyliodine diacetate and molecular iodine: Synthesis of 2-hydroxy-2-aryl/alkyl-2,3-dihydroquinolin-4(1H)-ones. *Tet. Lett*. 62: 152631.

Kidwai, M., Bansal,V., & Mothsra, P. (2007). Molecular iodine: A highly efficient catalyst for the synthesis of 7-

arylbenzopyrano[1,3]diazepines in non-protic solvents. *Journal of Molecular Catalysis A: Chemical*. 266: 43–46.

Kim, S.W., Um,T.W., & Shin, S. (2018). Metal-Free Iodine-Catalyzed Oxidation of Ynamides and Diaryl Acetylenes into 1,2-Diketo Compounds. *J. Org. Chem*. 83(8): 4703–4711.

Luo, W. K., Shi, X., Zhou, W., & Yang L. (2016). Iodine-Catalyzed Oxidative Functionalization of Azaarenes with Benzylic C(sp3)–H Bonds via N-Alkylation/Amidation Cascade: Two-Step Synthesis of Isoindolo[2,1-b]isoquinolin-7(5H)-one. *Org. Lett*. 18: 2036–2039.

Margarita, S. C., Igor, V. B., Zoya, A. S., Alexander, Y. T., & Tatiana, S. K. (2013). Spectroscopic and structural study of novel interaction product of pyrrolidine-2-thione with molecular iodine. Presumable mechanisms of oxidation. *J. of Mol. Struc*. 1047: 204–208.

Rok, P.L., & Stojan, S. (2014). Aerobic oxidative a-iodination of carbonyl compounds using molecular iodine activated by a nitrate-based catalytic system. *Tet. Lett*. 55: 5643–5647.

Ryosuke, O., Misato, T., & Hideo, T. (2010). Metal-free one-pot oxidative conversion of benzylic alcohols and benzylic halides into aromatic amides with molecular iodine in aq ammonia, and hydrogen peroxide. *Tet. Lett*. 51: 4378–4381.

Shantharjun, B., Rajeswari, R., Vani, D., Unnava, R., Sridhar, B., & Reddy, K. R. (2019), Metal-Free, One-Pot Oxidative Triple Functionalization of Azaarenes with Methyl Arenes Mediated by Molecular Iodine/TBHP: Synthesis of N-Benzylated Iodo(iso)quinolinones. *Asian J. Org. Chem*. 8: 1–11.

Sharma, K. K., Patel, D. I., & Jain, R. (2015), Metal-free synthesis of N-fused heterocyclic iodides via C–H functionalization mediated by tert-butylhydroperoxide. *Chem. Commun*. 51: 15129–15132.

Sun, K., Lv, Y., Wang, J., Sun, L., Liu, M., Jia, X., Liu, Z., & Li, X.; (2015). Wang, Regioselective, Molecular Iodine-Mediated C3 Iodination of Quinolines. *Org. Lett*. 17: 4408–4411.

Tang, S. Kun, L., Yue, L., Xinlong, G., Meng, G., & Aiwen, L.; (2015). Iodine-Catalyzed Radical Oxidative Annulation for the Construction of Dihydrofurans and Indolizines; *Org. Lett*. 17(10): 2404-2407.

Vivek, T. H., & Pradeep, D. L. (2014). A metal-free protocol for direct oxidative de-alkoxycarbonylation of alkyl phenyl acetate by molecular iodine. *Tet. Lett*. 55: 2337–2339.

Xia, W., Xiao, G., Peng, Z., Yan-dong, W., & An-xin, W. (2017). Iodine-Catalyzed Oxidative Coupling To Construct C−O Bonds for the Synthesis of 2,3-Dihydrooxepines. *Org. Lett*. 19(17): 4584-4587.

Xianglin, L., Runfa, H., Qiang, L., Yanping, G., Jingqing, L., Xiuwen, C., Zhongzhi, Z., Yubing, H., & Yibiao, L. (2020). Metal-Free Oxidative Esterification of Ketones and Potassium Xanthates: Selective Synthesis of α-Ketoesters and Esters. *J. Org. Chem*. 85: 5220−5230.

Xu, H., Weng, Y., M., Chen, H., & Zhang, Z. (2020) Unexpected Iodine-Promoted Aerobic Oxidation of α-Cyano-δ-keto Esters: A Facile Synthesis of α,δ-Dicarbonyl Esters. *Synthesis*. 52: 1841-1846.

Xue, W. J., Gao, Q. H., & Wu, A. X. (2015). Molecular iodine mediated oxidative cross-coupling of sp3 C-H with sp2 C-H: direct synthesis of substituted indolo[2,3-b]carbazoles via formal [2+2+1+1] cyclization. *Tet. Lett*. 56(51): 7115-7119.

Yadav, V. K., Vishnu, P., Srivastava, L. D., & Yadav, S. (2016). Molecular iodine mediated oxidative coupling of enol acetates with sodium sulfinates leading to β-keto sulfones. *Tet. Lett*. 57(21): 2236-2238.

Zheng, J. Q., Ying, L., Zhong, J. W., Zhang, Z., Yu, X. D., & Xi, C. W. (2013). Molecular iodine-mediated S–N and C–N cross-coupling and oxidative aromatization of 3,4-dihydropyrimidin-2(1H)-thiones with secondary amines. *Tet. Lett*. 54: 1884–1887.

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