2. INTRODUCTION

The reaction of various brominating reagent with alkali metal alkynylides represents another general entry into alkynyl bromide. Several brominating agents have been reported in the last two decades. Actually bromination is a fundamental transformation in organic chemistry. The review of literature explores the critical point of current knowledge on a particular topic and expresses the interest of research. In other words, the literature review is a single summary of the sources; usually it has a directorial pattern and syndicates both synthesis and summary about the research. The reviews of literature relevant for the study are presented as following.

2.1 The bromination of activated aromatic substrates and acylation of alcohols using PEG KBr₃:

Dey and Dhar (2013) testified a new synthesis system, PEG KBr₃ (polyethylene glycol reinforced potassium tribromide) besides they reported its application in bromination and acylation reactions. The \((\text{NH}_4)_3\text{PO}_4\) oxidizes potassium bromide to the corresponding tribromide which is entrapped by polyethylene glycol prominent to a stable PEG KBr₃. This reagent system is highly efficient for bromination of activated aromatic substrates and acylation of wide range alcohols. The reaction method is ecologically-friendly and doesn’t involve any toxic and hazards reagents/solvent.

\[
\text{R} \quad \text{PEG KBr}_3 \quad \underset{\text{r.t.}}{\rightarrow} \quad \text{R} \quad \text{Br}
\]

Where \(R= -\text{NH}_2, -\text{NHR}, -\text{OH}, -\text{OMe}\)
2.2 N-Bromosuccinimide:

Heropoulos et.al (2007) studied many bromination reactions with N-bromosuccinimide under microwave irradiation or high-intensity ultrasound, in aqueous and non-aqueous medium of various aromatic compounds. They reported diverse chemoselectivity in microwave and ultrasound assisted bromination reactions of various alkylaryls with NBS, in both neat and aqueous. As a result, microwaves give both side-chains a bromination and ring substitution, whereas ring substitution occurs in water with ultrasound only.

With the non-aqueous reaction method, side-chain a-bromination dominates for microwave supported reactions. In aqueous medium, the chemoselectivity with microwave-promoted bromination is quiet similar to the traditional methods reported.

![Chemical reaction diagram](image)

A clean eco-friendly, fast, simple, regioselective, and economically competitive method for synthesis of benzyl bromide from toluene by two-phase electrolysis through electrochemical route were studied by Raju et.al (2006).

Toluene was electrochemical brominated in an undivided cell at the temperature of 0 °C and the process parameters were studied and optimized. In this process 98 percent conversion was observed and yield was found to be 94 percent.
In order to improve their thermal stability, PCHD homopolymer, diblock co-polymer of PCHD with styrene (PCHD-b-PS), and crosslinked PCHD membranes were dehydrogenated by addition of bromine to the polymer in solution, followed by dehydrobromination using an isothermal treatment at elevated temperature.

The characterization of the obtained brominated PCHD materials done by thermogravimetric analysis (TGA) and FT-IR before and after dehydrobromination process.

It was that dehydrobrominated PCHD samples were characterized using elemental analysis and it was observed that some aromatization did occur and thermal stability of the treated polymer was enhanced when compare with its PCHD precursor. However the dehydrogenation of PCHD to polyphenylene was not complete.

This kind of compounds may be an interest as high carbon content, films like graphene\(^ {32} \).

Diblock co-polymer of PCHD with styrene and cross-linked PCHD membranes were processes through the same bromination method, which resulted in significantly enriched thermal stabilities for mentioned compounds as well. (Huang et.al 2012).
2.3 Bromination of alkynes and alkenes:

The arenes were brominated by vanadium catalyst in the presence of a bromine salt and a Brønsted acid or a Lewis acid under molecular oxygen, and is considered as sustainable bromination method as compared to conventional bromination which is done with bromine. Bromination of alkenes and alkynes could be done by utilizing this catalytic reaction in order to give the analogous vic-bromides.

Instead of Brønsted acid, the use of aluminum halide as a Lewis acid was found to give more practical protocol for the oxidative bromination.

So here AlBr₃ serve both as a bromide source as well as a lewis acid in order to induce bromination fast and efficiently. 51V NMR experiment with the molecular oxygen act as a terminal oxidant shows the flexible redox cycle of the vanadium species.

This methodology as a catalytic system is additional advantageous than vanadium bromo peroxidase (VBrPO) dictating hydrogen peroxide as an oxidant. (Kikushima et.al 2010)
2.4 Synthesis of Arylboronic Esters:

Leng et.al (2011) described an effective and facile synthesis of arylboronic esters having benzoxazole moiety by the use of a novel family of palladacycle i.e. Cyclopalladated ferrocenylimines catalysts. The whole reaction took place in two steps.

The first one is the bromination of 2-arylbenzoxazoles and the second one is subsequent borylation. The bromination of p-CeH bond, using NBS as the brominating reagent was an electrophilic substitution process, and the brominated products were determined by HMBC (1H-detected heteronuclear multiple bond correlation) spectra.

They found that the p-position of the N-atom in the benzene ring of benzoxazole was the main site of bromination reaction. Furthermore in borylation reaction, the of bromination of CeH bonds and and successive borylation took place in an effective manner and the borylated products will be used in traditional Pd (0)/Pd (II) coupling reactions to afford the complicated p-conjugated systems with benzoxazoles moieties.

2.5 Hexamethylenetetramine–bromine (HMTAB).

Heravi et.al (2005) concluded and developed a highly efficient and regioselective method of bromination for aromatic compounds in which stoichiometric amount of hexamethylenetetramine–bromine (HMTAB) was used as an effective reagent in dichloromethane.
They reported that the selectivity depends on the temperature and nature of the substituent on the substrate. The reactivity of this reagent was increased when it was supported by silica gel for the bromination of less activated compounds.

![Chemical reaction](image)

A very fast, regioselective and efficient method has been established by Li et al. (2007) for the bromination of isoxazoles and pyrazoles using microwave irradiation. In this process, according to the reactivity of the substrates, N- bromosuccinimide was used in different acid solvents in order to give pyrazoles and mono-brominated isoxazoles in good yields.

Trifluoroacetic acid found to be the best solvent for the bromination of highly unreactive isoxazoles and pyrazoles the several advantages including short reaction times, enhanced yields, and operational simplicity were reported by this process. Isoxazoles and pyrazoles were also iodinized in good yields by this method.

2.6 Aprotic solvents and bromination:

Rayala and Wnuk (2012) reported that treatment of the protected and unprotected nucleosides with 1,3-dibromo-5,5-dimethylhydantoin in aprotic solvents such as CH₂Cl₂, CH₃CN, or DMF effected smooth bromination of uridine and cytidine derivatives at C-5 of pyrimidine rings as well as adenosine and
guanosine derivatives at C-8 of purine rings. Addition of Lewis acids such as trimethyl silyl trifluoromethanesulfonate enhanced the efficiency of bromination.

2.7 Oxibromination of selected pharmaceuticals:

Five selected pharmaceuticals including naproxen, metoprolol, amoxicillin, hydrochlorothiazide and phenacetin were brominated individually by dissolving these compounds in ultra-pure water. It was observed that highest rate of bromination was seen for the amoxicillin and intermediate rate for reaction was observed for naproxen however the rate of reaction was slow for other three remaining pharmaceuticals.

The bromination rate was confirmed by the $k_{app}$ values that confirms the strong influence of pH. In simultaneous bromination of three water matrices, it was observed that the elimination decreased in the sequence PZ > PA > BA, which was in accordance with the sequence of increasing NOM present. As there is low concentration of bromide in waste waters and drinking waters, it slightly accelerates the oxidation of the selected pharmaceuticals during chlorine disinfection. (Benitez et. al, 2011)

2.8 Photo-bromination reactions in sunlit saline surface waters:

Salicylic acid can experience photo-bromination reactions in sundrenched brine surface waters as overburdened and stated by Tamtam and Chiron (2012) during their combination of field and laboratory experimentation.

There is a significant prospective of Brine water for photochemical realization of brominated compounds in case when Salicylic acid is castoff as resultant compound. They reported that one of the most environmental-friendly significant transformation pathways in saline water is Photo-chemically prompted bromination owed to the formation of extremely hazards and toxic brominated compounds.

They had conducted Laboratory experiments which revealed that most significant
environmental indicators for the occurrence of these processes were nitrite, ammonium and CDOM levels that coastal lagoon and nautical waters overlapping the photic region and receiving treated WWTP wastes are the most vulnerable waters.

Nitrite acts as a photolytic source of $\cdot$OH and NO$^\bullet$, whereas CDOM as a photolytic source of $\cdot$OH and O$_2$$^•$$. $\cdot$OH accounts for the realization of reactive brominated species (Br$^\bullet$, Br$_2$$^•$), acting as straight brominating agents of Salicylic acid. NO$^\bullet$ might react thru O$_2$$^•$ to yield peroxynitrite, which is capable to oxidize bromide ions into HOBr, resulting in a novel brominating pathway for SA, which stayed found to be catalyzed by ammonium.

However, difficult analysis with highly accurate measurements of in-situ peroxynitrite at different depths in the H$_2$O column would be requires, in their later supposition.

### 2.9 Bromide as reagent:

Four different aromatic compounds including two phenols and two anisole’s were brominated in a cationic surfactant based microemulsion using the bromide as reagent.

Dilute nitric acid was used to oxidize bromide ion to elemental bromine which in turn reacts with the aromatic compounds and the results have been compared with two-phase procedures using either an in situ-prepared or a pre-prepared complex between bromine and a quaternary ammonium salt which was used as an oxidizing reagent.

They reported that when reaction was performed in the micro emulsion, it brought an easier, safer and more selective p-bromination.

**Georgi et. al. (2007), reported a** microwave and ultrasound assisted bromination of alkyl aromatic compounds. However, this protocol was not very effective for commercial operations. Here is the outline concept of the protocol.
Further they found and reported that for the preparation of brominated aromatic compounds, micro emulsion based on a surface-active quaternary ammonium bromide can be used as an environmentally benign, efficient, safe, and easy reaction system. (Currie et. al, 2003)

Two –phase reactions:

1. In-situ prepared bromine salt:

2. Pre-prepared bromine salt:

A defensible brominating agent was proposed especially more effective for toluene.
There are two phases in proposed protocol in presence of different catalytic approaches.

First phase in presence of vanadium V (V) and second phase with Molybdate Mo (VI), where H$_2$O$_2$ is a primary oxidant and KBr reacts as a source of active bromine. By using toluene as solvent, the effectiveness of reaction can be improved and toluene PhCH$_2$Br achieved in a good quality yield. Here the advantage is that catalytic phase can be recycled in a very effective manner.

2.9.1 Vanadium and molybdenum as halogenating reagent:

Galloni et.al reported a method of oxidative bromination for toluene by using cost effective oxidant’s like H$_2$O$_2$ and in a very mild reaction media apart from nature of solvent.

As an effective and ecofriendly approach KBr was used as a source of bromine. But the main concern is to eliminate the environment hazardous and non-value adding substances from the process of cost effective route to recycle these. Which can improve the efficiency of catalytic system particularly with molybdate (IV) catalyst.

As a substitute benzyl bromides are the best choice as a substrate for further use in such synthetic protocols and procedures, the present protocol is possible with some other benzyl substrate also. But there are no such data available for methodology scope and technology transfer.

2.9.2 Preparation of Venlafaxine (IX):

According to Rathod et.al. (2003) processes for the preparation of Venlafaxine (IX) via the novel epoxy-nitrile intermediate (I), which when subjected to hydrogenation forms compound (X). This research relates to a novel intermediate which is a valuable addition in the synthesis of a well-known medicament by a more advantageous route.

The discovery further connects to processes by which such an intermediate my first be prepared itself and thereafter may be converted in to the known anti-depressant compound Venlafaxine which is pharmacologically acceptable worldwide.
Venlafaxine selectively constrains the neuronal acceptance of serotonin-norepinephrine and to a reduced extent dopamine. It seems to be as efficient as standard anti-depressant like imipramine.

Venlafaxine's unique chemical structure and neuro-pharmacological activity give it a broader spectrum of activity than other antidepressants. These known traditional synthetic routes incline to comprise the use of hazardous, toxic, expensive and moisture sensitive reagents.
Fig. 2.1 Synthesis of Venlafaxine (IX)
The brominated phenolic compounds are very important materials from the point of view of antiseptic hygienic and disinfectant character and they are also useful in industry for manufacturing biologically active agrochemical, antioxidancy and flame retardancy.

2.9.3 Quinoxalinium bromochromate:

Değirmenbaşi and Ozgün (2006) reported that quinoxalinium bromochromate is a versatile and practical reagent for the oxidation of alcohols as it has lower acidity, ready and easy preparation method, stable, non-hygroscopic, easily work up with the reaction mixture, gives reasonable good yields of products and take less reaction time. Due to all these characteristics it is considered to be a good brominating agent for selective aromatic compounds and a very useful addition to the presently available bench reagents in organic synthesis.

2.9.4 Preparation tefluthrin from 2, 3, 5, 6-tetrafluorodimethylolbenzene:

According to Rathod et.al. (2003) processes for the preparation of Venlafaxine (IX) via the novel epoxy-nitrile intermediate (I), which when subjected to hydrogenation forms compound (X), and may subsequently be reduced to yield the desired product (IX).

The epoxy-nitrile intermediate (I) itself may be synthesized via various alternative reaction strategies, from a range of starting materials. E.g. 4-methoxy-benzaldehyde (VI), upon treatment with cyclohexyl magnesium bromide yields compound (V). This in turn may be oxidized to yield compound (III), which forms compound (II) on treatment with an (x-keto-halogenation agent. Cyanation of compound (II), then yields the desired epoxy nitrile intermediate (I), from which Venlafaxine (IX) may be synthesized.

The brominated phenolic compounds are very important materials from the point of view of antiseptic hygienic and disinfectant character and they are also useful in industry for manufacturing biologically active agrochemical, antioxidancy and flame retardancy. 1-Benzyl 4-aza-1-azoniabicyclo [2.2.2] octane tribromide has been...
examined over several phenolic compounds under mild conditions. The reaction gives brominated phenols in good to excellent yields. *(Hajipour, 2006)*

Methods for preparing 2, 3, 5, 6-tetrafluorodimethylolbenzene, an intermediate for the preparation of pyrethroids, are disclosed by *Wang and Jiang (2007)*. They discussed that the method for preparing 2, 3, 5, 6-tetrafluorodimethylolbenzene includes the reduction of tetrafluoroterephthalate.

Various reduction processes are disclosed, which are simple and safe and can afford the product in high yield and purity. Processes for preparing tefluthrin from 2, 3, 5, 6-tetrafluorodimethylolbenzene, by *halogenation*, hydrogenation, and esterification, are also disclosed.

### 2.9.5 Lewis Acid:

*Mukhopadhyay, et al. (2008)* described a method fluorinated organic compounds preparation in which at least one fluorinated olefin in gas-phase is reacted with methyl fluoride in the presence of a Lewis Acid catalyst in order to form a product that at least have 3 carbon atoms.

### 2.9.6 NaBr and NaI, halogenating reagent for aromatics:

*Firouzabadi et.al. (2009)* found that various aromatic compounds were brominated and iodinated with sodium bromide and NaI using oxone (2KHSO₅·KHSO₄·K₂SO₄) in H₂O, both are considered as a safe source of halogens which is another advantage of this protocol and it can be applicable easily to the large scale industrial processes or operations.

The method has been successfully used for iodocyclization of an unsaturated carboxylic acid and alcohol in high to excellent yields through direct bromination process. The usage of NaBr and NaI as the safe sources of halogens is another advantage of the protocol.
2.9.7 Terminal oxidant (H$_2$O$_2$):

**Firouzabadi et.al. (2009)** reported a novel and environment friendly catalytic method in which hydrogen peroxide was used as terminal oxidant for the efficient monoiodination and bromination of arenes as well as iodoetherification and iodolactonization of olefins.

The process rely on use of sodium iodide or sodium bromide, cerium (III) chloride and hydrogen peroxide (35 percent) as an effective catalyst in aqueous medium at room temperature or under reflux conditions.

The iodination of anilines was carried out using this procedure with high regioselectivity at the p-position with the formation of small amounts of the ortho isomers. However, anilines were brominated with absolute regioselectivity to give p-isomers as the sole products in high to excellent yields.

Similarly, toluene, m-xylene, chloro- and bromobenzens etc. were iodinated and brominated with excellent regioselectivity in order to produce the p-isomers as the sole products. Monohalogenated benzene in good yields was obtained by halogenation of benzene using the catalytic system. Olefins can also be used for the iodolactonization and Iodoetherification to get high yields at room temperature. However, the bromination of olefins by this protocol failed and the starting materials were detected intact.

3. Halogenating reagents:

**Zhdankin (2009)** disclosed that there is a growing interest of industrial chemists in iodine (III) compounds because it has very useful oxidizing properties, and is available commercially and is environmental friendly. A big demand of activity in numerous areas of the hypervalent iodine chemistry has been fingered.

These areas covers the application of hypervalent iodine reagents in various oxidative transformations, the development and synthetic use of polymer- supported and green hypervalent iodine reagents, and the catalytic applications of organoiodine compounds.
Fong, et al. (2009) reported that it is a direct process of preparing alkyl alcohol alkoxylates from the alkyl halides because in this reaction process it’s directly achieving final products without any intermediate formation of compound/product. In reaction mechanism followed by a catalytic system coupling of alkyl halides took place with the nucleophilic material in order to achieve the final products.

However, these must be a one metallic homogenous catalytic system which actually forms a bonding between metal and halogen during the reaction mechanism process. Further, they have also described the process of converting alkanes (paraffin’s) to alkyl alcohol alkoxylates is also described.

The whole reaction involved two steps. In first step halogenation of at least one alkyl halide. In second step a portion of alkyl halide coupled (through direct alkoxylation process) with a nucleophilic material in the presence of a homogeneous catalytic system. In order to produce alkyl alcohol alkoxylates.

3.1 Electrochemical bromination of germacrene D

Takahisa et al. (2004) reported an electrochemical bromination of germacrene D and provide a very value adding reagent system protocol for halogenation of germacrene D1 and geraniol 2. This process for bromination is very efficient and environmentally benign technology. They introduced the biosynthesis approach by using germacrene 1 in figure 2.1.
Fig. 2.2 Biosynthesis by using germacrene D1.

They also converted germacrene D1 into a bicyclic derivative 6. Other than brominated product 6, some other brominated compounds also achieved and numbered as 3, 4, 5, 7, 8, 9, and 10. They expressed the route in figure 2.2.
According to Koyano et al. (2009) the development provides a process for synthesis of 2, 3, 4-trifluoro-5-iodo and 2, 3, 4-trifluoro-5-bromo benzoic acid, the process comprising a halogenation step in which direct iodination or bromination of 2, 3, 4-trifluorobenzoic acid is performed with an halogenating agent in a process solvent in the presence of an oxidizing agent.

According to the invention, there is provided a procedure for suitable production of 2, 3, 4-trifluoro-5-iodo and 2, 3, 4-trifluoro-5-bromo benzoic acid in great yield and purity in a highly regioselective manner.

T. Raju et. al (2005) expressed a new technique for bromination of toluene by using electrochemical system they have reported synthesis of benzyl bromide in a two phase process using toluene as reactant. This complete reaction protocol followed at zero °C and achieved a high conversion rate of 94-96 percent. They also noticed effect of temperature on yield for protocol.
Kumar et.al (2011) introduced an aq. CaBr₂-Br₂ new reagent system as very efficient, instant, economical and ecologically safe for halogenation of aromatics following green approach and briefs the reactivity of it. They found the reagent very useful for acetylation of alcohols. In short this reagent system was a value addition to existing halogenating reagents. Cetylpyridinium tribromide (CetPyTB) as a reagent is more valuable addition to chemical, pharmaceutical, polymer etc. industries.

Izumisawa and Togo (2011) found that when -bromoketone was obtained in good an ionic liquid such as [bmim]PF6 was used, yields with good purity (>80 per cent) by simple ether extraction of the reaction mixture and the ionic liquid reaction medium could be reused for the same reaction up to the 7th time while maintaining the high yields of α-bromoketone. The alpha-bromination of β- dicarbonyls and cyclic ketones with NBS in ionic liquids, and the aromatic ring bromination with NBS in ionic liquids have been reported as well.

However, to the best of our knowledge, there are no synthetic studies that deal with the preparation of thiazoles from ketones with NBS and thioamides in ionic liquids. Here, as a part of our synthetic study of ionic liquids, we would like to report the preparation of alpha-bromoketones and thiazoles from ketones, with NBS and thioamides in typical room-temperature ionic liquids.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Temperature (°C)</th>
<th>Toluene (mmol)</th>
<th>Benzyl bromide (mmol)</th>
<th>Yield (%)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>19</td>
<td>18</td>
<td>94</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>19</td>
<td>15</td>
<td>79</td>
<td>40</td>
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<td>3</td>
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<td>30</td>
<td>19</td>
<td>14</td>
<td>76</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>19</td>
<td>13.4</td>
<td>70</td>
<td>34</td>
</tr>
</tbody>
</table>

**Table 2.1** Effect of temperature on yield of final product.
Miller and Moens (2011) reported a method comprising reacting an alkane gas with a halogen gas in a halogenations reactor to form a halogenation reaction product mixture comprising alkane halide and hydrogen halide mixture; mixing the halogenations reaction product mixture with a countercurrent flow of a metal organic salt thereby forming an extractor product mixture of a metal halide, organic salt, and organic acid separating the organic ester and organic acid mixture from the metal halide.

Oxygenating the metal halide to form a metal oxide and halide containing gasses; separating the metal oxide from the halide containing gasses; mixing the metal oxide with water to form a metal oxide slurry; mixing the metal oxide slurry with a countercurrent flow of the organic ester and organic acid mixture to form a raw product comprising alkanol, a metal organic salt is provided.

An integrated process for the solution polymerization and subsequent Halogenation of butyl rubber in a common medium is disclosed.

The process comprises providing a solution polymerization reactor containing a C6 medium mixed with a monomer mixture comprising at least an isoolefin monomer and a multiolefin monomer in a mass ratio of monomer mixture to medium of from 61:39 to 80:20. Once polymerized, residual unreacted monomer mixture is separated from the rubber solution using a distillation process.

The residual monomers may then be purified and recycled back into the reactor. The separated rubber solution is then halogenated. The process obviates the need for separating the rubber from the medium following polymerization, then re-dissolving it in another solvent for halogenation, thereby saving energy cost. The process optionally employs heat exchangers for the reactor feed streams to further reduce energy consumption. (Paul et. al., 2011)

Elnagar and Hassan (2011) described the invention that gives a procedure for the N-halogenation of at least one 5-hydrocarbyl hydantoin and/or at least one 5,5-dihydrocarbyl hydantoin. The whole process consists of feeding chemicals in reaction zone which is as follows (i) First of all inorganic base, 5,5-
dimethylhydantoin and water all these fed either separately or in any combination(s), (ii) A brominating agent is fed separately (iii) Thereafter a chlorinating agent was fed separately in such a proportion so that either during all the time or substantively, halogenation of 5,5-dihydrocarbyl hydantoin and 5-hydrocarbyl hydantoin occurs and the prepared halogenated product get precipitated in this liquid phase of aqueous reaction mixture.

Further the pH of the liquid phase of this reaction mixture is maintained in the range of 2-8, continuously or substantively continuously during the all or substantively all of the time the concurrent feeding is done.

By this invention a composite matter of halogenated 5-hydrocarbyl hydantoin or a halogenated 5,5-dihydrocarbyl hydantoin, which is a mixture of the 1,3-dibromo-, 1,3-dichloro-, and/or N,N’-bromochloro-species of the halogenated hydantoin obtained.

Demet et al. (2008) introduced a new method for norbornene derivatives bromination. This protocol is effective for synthesis of nonbornanes and nonbornenes. All reactions were performed at low temperature and reactivity studied and reported, rise in temperature effect the yield of end product. In benzonorbornadiene gives a single rearrangement product, the route was explained in scheme C.
Meneguzzo et al (2011) reported the method for this synthesis of aromatic alpha-hydroxyketones (aromatic $\alpha$-hydroxyketones) that does not require the use of chlorine, sulfuryl chloride or bromine and comprises the halogenation of an intermediate aromatic ketone with a hydrogen halide in the presence of an oxidizing compound.

Mezei et al (2011) introduced a unique general halogenated formula (III) and method, wherein R was represented as fluorine or chlorine atom and X characterizes chlorine or bromine atom. The initial reactant or general halogenated formula (II) was cyclopropyl benzyl ketone.

In which R was ‘F-atom’ or ‘Cl-atom’ and the process of halogenation were carried out in aqueous H$_2$O$_2$ and hydrogen halide in existence of polar solvent or in different route process of halogenation was carried out between aq. hydrogen halide and sulphuric acid. But the only drawback of the process is that it has its limitations and only value addition to commercial scale operations.
Lukas et al (2011) explained a unique synthetic protocol for fluorination of β-ketoesters by using titanium TADDOLate. Technology is good for commercial processes because it gives enantiomeric excess up to 91 Percent.

![Synthetic protocol for fluorination of β-ketoesters](image)

**Fig. 2.5** Synthetic protocol for fluorination of β-ketoesters
\[
\begin{align*}
\text{Cl} \quad \text{N}^-_\text{F} \quad 2 \text{BF}_4^- \\
\xrightarrow{(F-\text{TEDA}; 1.15 \text{ equiv})} \\
\text{K1 or K2 (5 mol %)} \\
\text{MeCN, rt} \\
\xrightarrow{\text{K1 or K2 (5 mol %)}} \\
\text{R} \quad \text{Me} \quad \text{F} \quad \text{Me} \\
\quad \text{R}' \\
\quad + \text{H-TEDA}
\end{align*}
\]

**chiral Lewis acid catalysts:**

\[
\begin{align*}
\text{[(R,R)-K1]} \\
\text{[(R,R)-K2]}
\end{align*}
\]

**a)**

\[
\begin{align*}
\delta (1H) & \quad 6.0 \quad 4.0 \quad 2.0 \quad \text{ppm} \\
1 & 1-F \\
1-F & 1 \\
1-F & 1 \\
1-F & 1 \\
1-F & 1
\end{align*}
\]

**b)**

\[
\begin{align*}
\text{blank} & \quad \text{Cp}_2\text{Ti(OTf)}_2 & \quad \text{HBF}_4 & \quad \text{BF}_3 & \quad \text{Cp}_2\text{Zr(OTf)}_2
\end{align*}
\]

Review of Literature
Johnson, et al. (2011) discusses the synthesis processes of the fluorinated olefins which were used preferably for the commercialization of CF₂CF₂CH₂ (1234yf). In this process firstly a compound of preferred embodiments Formula (IA) C(X)₂CF₂CCl₃ was exposed here each X is independently Cl, F, or H, and the compound will be CCl₂CF₂CCl₂, to one or more sets of reaction conditions, but rather a substantially single set of reaction conditions, efficient in production of at least one chlorofluoropropane, rather in accordance with formula (IB): CF₂CClX'C(X').₃ Formula (IB) where each X' is individually Cl, F or H, and then revealing the compound of Formula (IB) to one or extra sets of reaction conditions, but rather a significantly single set of reaction conditions, efficient to manufacture a compound of Formula (II) CF₂CF₂CH₂ where Z is H, F, Br, Cl or I. Effect of solvent content also explained.

Chiu et al; (2011) described a method for producing 1, 1, 1, 2- tetrafluoropropene and/or 1, 1, 1, 2, 3-pentafluoropropene using a single set of four unit operations, the unit operations being (1) hydrogenation of a starting material comprising hexafluoropropene and optionally recycled 1, 1, 1, 2, 3- pentafluoropropene; (2) separation of the desired intermediate hydrofluoroalkane, such as 1, 1, 1, 2, 3, 3-hexafluoropropene and/or 1, 1, 1, 2, 3-pentafluoropropene; (3) dehydrofluorination of the intermediate hydrofluoroalkane to produce the desired 1,1,1,2-tetrafluoropropene and/or 1, 1, 1, 2, 3-pentafluoropropene, followed by another separation to isolate the desired product and, optionally, recycle of the 1, 1, 1, 2, 3-pentafluoropropene.

The invention made by Ten Kate et al. (2012) reported a process of catalytic halogenation of an organic compound that has at least one vicinal diol moiety. In this reaction process the organic compound reacts with the hydrogen halide in the
presence of a catalyst, where an organic compound is also comprised a \( \beta \)-keto aldehyde moiety or a \( \beta \)-diketone moiety.

![Catalytic halogenation of an organic compound that has at least one vicinal diol moiety](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>K1 (mol %)</th>
<th>T (°C)</th>
<th>Additives (mol %)</th>
<th>t (h)</th>
<th>ee (%)</th>
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<tbody>
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<td>rt</td>
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\( ^a \)All reactions were performed in reagent grade acetonitrile stored over 3 Å molecular sieves and run to complete conversion (TLC), unless otherwise mentioned. \( ^b \)Reaction stopped before complete conversion. Entries 1-5 vs 7-11 vs 12-15 were run with different batches of F-TEDA, solvent and catalyst, leading to small selectivity deviations under seemingly identical conditions. \( ^c \)50% conversion. \( ^d \)No reaction. \( ^f \)Conversion stopped at 80%.

**Fig. 2.6** Catalytic halogenation of an organic compound that has at least one vicinal diol moiety

**Kumar et al. (2011)** in this study they taken an “aqueous CaBr\(_2\)-Br\(_2\) reagent system” as a fast and innovative brominating agent system” for the direct bromination of various aromatic compounds of industrially and pharmaceutically importance. They reported that molecular bromine in solution is used for the bromination reaction of anilines and phenols that ultimately resulted in process of polybromination. The product that has been brominated rather than undergoing substitution get oxidized due to the presence of oxidants.
In some cases it requires protection of the -NH$_2$ group. Further they reported facile, instantaneous, and regiospecific bromination of substituted phenols, anilines, anilides and aldehydes of industrially significant, under ambient conditions that resulted in considerable yields with highest in purity. The hydrogen bromide i.e. byproduct waste can be used efficiently and the brominating agent has also been invigorated and recycled in successive bromination processes without any substantial forfeiture of the product/reagent reactivity.

Further they reported a facile, regiospecific and instantaneous bromination of substituted phenol, anilines, anilides and aldehydes. They have discussed and reported the synthesis of largest selling flame retardant with high commercial importance through a practical and industrially workable route. For the first time potassium tribromide was used as an efficient brominating agent tetrabromobisphenol A for the bromination of bisphenol A. The whole reaction took only 5-10 minutes at a very ambient temperature and the yield obtained 99 percent with high purity more than 99 percent.

Further the reaction process is free from reaction byproduct wastes and does not have more ionic impurities. Further during the bromination reaction the produced hydrogen bromide can be used for the preparation of various values added brominated products or can be disposed of as waste but this will cause serious ecological threats/complications.

Gupta et al (2009) reported a new stabilizer (A combination of hydrotalcite, zeolite, calcium stearate, and magnesium acetylacetonate). In plastic and polymer industries, there is a big matter of concern due to unwanted degradation and discoloration of poly vinyl chlorode at processing temperature.

In order to explore the probable mechanism of stabilization for various commercial syntheses as per market and environmental regulatory demand, a new combination of reagent /stabilizer system has been reported.

The visual color examination for color stability has been reported and thermal behaviors analyzed in terms of released HCl as a process waste. To study, color
stabilization in high temperature reactions and processes “Oven aging method” was used. Formulation of Poly Vinyl Chloride sheets by different synthetic routes using lab coater is subjected to oven for different time interlude.

The spectroscopic studies done by using UV-vis spectroscopy for color development during oven aging method.

The recorded spectral data by UV-vis method confirms that pale yellow color appears due to presence of average sized polyenes within the PVC. Whereas, the range between (n=10-14) gives red and brown color respectively.

The phenomenon, ion exchange and absorption have been directed by mechanism of stabilization, which confirms that ion exchange and adsorption are responsible for hydrotalcites as long term stabilizers. The inhibition of acetyl acetonate complex, which is a substitute compound of allylic chlorides, plays a key role in formation of long-chain polyene responsible for darkening in polymer industries.

Hintermann L. et al (2011) reported Asymmetric catalysis with TADDOLato–titanium(IV) dichloride (TADDOL = α, α, α’, α’-tetraaryl-(1, 3- dioxolane-4, 5-diyl)-dimethanol) Lewis acids produces enantiomerically enriched α-fluorinated β-ketoesters in up to 91 per cent enantiomeric excess, with either F–TEDA (1-chloromethy 1-4-fluoro-1, 4-diazeniabicyclo[2.2.2]octane bis(tetrafluoroborate)) in acetonitrile solution or NFSI (N-fluorobenzenesulfinimide) in dichloromethane solution as fluorinating reagents.

The absolute configuration of several fluorination products was assigned through correlation. Evidence for ionization of the catalyst complex by chloride dissociation, followed by generation of titanium β-ketoenolates as key reaction intermediates, was obtained. Based on the experimental findings, a general mechanistic sketch and a steric model of induction are proposed.

Wang H. et al (2012) described that by using copper halide under mild conditions unprotected anilines can be chlorinated and brominated p-position. This process does not use any potentially hazards reagent and solvent. In other words we can say the method introduced by Wang is instant, mild and eco-friendly.
Paul S. et al (2005) reported that the synthesis of α-Bromoalkanones 2 can be followed by using alkanones 1 with Urea-Hydrogen peroxide-Sodium Bromide reagent system over SiO$_2$-acetic acid in solvent-free conditions. Urea-hydrogen peroxide is an alternative of 90 percent H$_2$O$_2$ and acts as a rich source of anhydrous H$_2$O$_2$. Use of UHP-NaBr seems to be very convenient in view of the above precedents.

This reagent system was quiet effective with complete utilization of Br$_2$ with minute ecological issues associated with the process as the reaction process waste is only H$_2$O. The UHP-NaBr reagent system over SiO$_2$-AcOH. Experimental condition has been carefully monitored to get maximum yield.

Kaushik, M.P. and Polshettiwar, V. (2006) introduced a new reagent system, which is quinolone (C$_9$H$_7$N) based ionic liquid. By this efficient and regioselective brominating reagent system N-octylquinolinium tribromide was in a good yield. A remarkable reactivity of Br$_2$ has been reported towards various substrates due to high active bromine content per molecule in the reaction process.

This is completely eco-friendly process because no organic solvent has been used in the reaction process. The octylquinolinium tribromide is a highly stable compound with safe source of Br$_2$ that’s why transportation and storage is very easy, which makes the process safe for industrial use. The effectiveness of this recycling and regenerating process was tested and found effective up to 6 cycles of process.

Aghapour, G. et al (2009) described an instant, regioselective and mild reaction process for the conversion of epoxides to β-chlorohydrins in a great yield. Even in the presence of tetrahydropropyranl ethers, amides, carboxylic acids, alcohols, oximes, and thiols by using chlorodiphenylphosphine ClPPh$_2$ as an reagent under solvent free and mild reaction conditions at 25°C temperature and a very short reaction time.

In this reaction process some functional groups remains intact, present in epoxide molecules by the reagent system like phenyl ring, C=C bond, ester groups etc.

Jagdale, A.R. et al (2009) reported that the α-halogenation of alkyl and aryl ketones with 1, 3-dichloro-5, 5′- dimethylhydration and NBS by using copper (II) triflate as
an effective reagent to give the corresponding $\alpha$-bromoketones and $\alpha$, $\alpha$-
dichloroketones with outstanding product selectivity and a high quality yield. In
conclusion for the first time Cu-catalyzed $\alpha$-halogenation of ketones in efficient and
simple manner was introduced.

In conclusion for the first time Cu-catalyzed $\alpha$-halogenation of ketones in an
efficient and easiest route was introduced. In continuation of the work on copper
triflate catalyzed transformations. The $\alpha$-chlorination of aliphatic ketones were
introduced with 1, 3-dichloro-5, 5-dimethylhydantoin catalyzed by Cu-triflate which
gave $\alpha$, $\alpha$-dichloroketones in 67-76 percent yields.

Kumar, A. et al (2011) described a very important functionalization transformation
of olefins by adding two different functional groups in a single step process.

Haloazidation is one of the most useful reactions for simultaneous introduction of
halogen and nitrogen functionality in to a carbon skeleton of an olefin. Haloazides
can be subjected to further synthetic manipulation to provide a new class of
functionalized organic compound such as vinyl azides, amines, aziridines, and
tetrazoles.

In literature, several methods have been introduced for iodozidation. However
unsteadiness and poor selectivity of iodoazides are the major problem associated with
these traditional methods.

Reddy, K.R. et al (2012) developed a highly efficient, instant, clean, mild reaction
condition, halogenation in good to excellent yields and high selectivity ultrasonic and
microwave assisted halogenation reaction of $\beta$-Naphthols in aqueous micellar
media.

It describes a set of green methods to acid, metal-ion free halogenation. The
reaction times were drastically reduced to few minutes under sonication and
microwave conditions from several hours of reaction time in traditional halogenation
reactions.
<table>
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<th>MWAR</th>
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Table 2.2 Bromination of Naphthols by H$_2$O$_2$-KBr in an aqueous micellar media

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Table 2.3 Chlorination of Naphthols by H$_2$O$_2$-KCl in an aqueous micellar media
Table 2.2 Iodination of Naphthols by H$_2$O$_2$-KI in an aqueous micellar media

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<th>Yield (%)</th>
<th>Selectivity (%)</th>
<th>Reaction Time (min)</th>
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<td>1.5</td>
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Fig. 2.7 Comparative study of reagent and reaction time for various aromatics in an AMM
This is an ecologically-safe, instant and highly safe regioselective procedure, which involved in-situ synthesis of activated halogens in presence of alkali halides.

A selective cationic category of surfactants such as cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) were found to facilitate efficiency of halogenation in aqueous media. In this reaction process H₂O also gives its remarkabiltiy, which catalyses chemical transformation b/w some organic insoluble-reactants.

However, results obtained under unanalyzed and micellar catalytic conditions are shown in Table No. 1, 2, 3 and Fig.1. Which indicates very high significance acceleration and followed by good quality yields. After achieving a very good success rate in Ultrasonic-assisted Organic Synthesis, we just tried to explore the opportunities in solvent free reaction conditions.

In solvent free reaction conditions rate of reaction accelerates in a very less reaction time. This boos-up in reaction was noticed due to grinding method which actually attributed high activation of molecules due to high conversion rate in mechanical energy by friction force applied between solid state reagents.

A very efficient and selective brominating system Br₂/SO₂Cl₂/Zeolite, has been introduced by Gnaim and Sheldon (2005). A selective and efficient p-bromination of chlorobenzene catalyzes by Ca₂⁺-Y zeolite reagent system at high conversion rate of end product approximately 89 percent and p-selectivity of 97 percent.

For synthesis of highly active brominating species, this reagent system is very effective because SO₂Cl₂ oxidizes hydrogen bromide and prevent its accumulation within the zeolite pores. The calcination regeneration process has been catalyzes by Ca₂⁺-Y in efficient mode. This reagent system and process can be used for other activated organic compounds like fluorobenzene, xylene, toluene etc.
The possible reaction process can be outlined in three steps of equations. In presence of zeolite and \( \text{SO}_2\text{Cl}_2 \) may react with bromine and give bromine monochloride and sulphur dioxide (eq.1), the similar reaction pattern follows in reaction of \( \text{Cl}_2 \) and bromine (eq.2).

To afford bromine \( \text{SO}_2\text{Cl}_2 \) may intact with hydrogen bromide and sulphur dioxide with HCl as represented in equation 3. As a result of reduction-oxidation reaction a new brominating agent bromine monochloride formed in both the cases followed by regeneration of bromine atom.

\[
\text{SO}_2\text{Cl}_2 (\text{I}) + \text{Br}_2 (\text{I}) \rightarrow 2\text{BrCl} (\text{I}) + \text{SO}_2 (\text{g}) \quad -------- (1)
\]

\[
\text{Cl}_2 (\text{g}) + \text{Br}_2 (\text{I}) \rightarrow 2\text{BrCl} (\text{I}) \quad -------- (2)
\]

\[
\text{SO}_2\text{Cl}_2 (\text{I}) + 2\text{HBr} (\text{g}) \rightarrow \text{Br}_2 (\text{I}) + 2\text{HCl} (\text{g}) + \text{SO}_2 (\text{g}) \quad -------- (3)
\]

Nishina and Takami (2012) has been introduced a new brominating reagent \( \text{Fe}_2\text{O}_3/\text{zeolite} \) for bromination of aromatic compounds but this reagent system was effective for bromination of non-activated aromatic compounds. The formation of catalytic species (\( \text{FeBr}_3 \)) was achieved in-situ form hydrogen bromide and \( \text{Fe}_2\text{O}_3 \).

This introduced reagent system was eco-friendly, easy to handle and storage, cost efficient and can be recycled by easy process. However, this reagent system can be amended to the carbon-carbon bond formation of benzene and one-post sequential bromination.
A simple ammonium deep eutectic solvent was cast off as a dual catalyst and eco-friendly reaction media for the bromination of 1-aminoanthra-9, 10-quinone, eliminating the need for volatile organic solvents and concentrated acids like H$_2$SO$_4$ as solvents or catalysts.

This simple ammonium deep eutectic solvent easily can be synthesized by using choline chloride and urea. It is comparatively economical and biodegradable, making it applicable for industrial applications.

The deep eutectic solvent was easily separated and reused without loss of activity, and thus provides a good alternative for industrial bromination of 1-aminoanthra-9, 10-quinone. \textit{(Phadtare and Shankarling, 2010).}
Adimurthy et.al. (2007) reported that mixtures of NaBr and NaBrO$_3$ in two different ratios (5:1) have been used for highly stereoselective bromination of alkenes and alkynes, and regioselective bromine substitution at the a-carbon of ketones and at the benzylic position of toluene derivatives.

The reactions were conducted in an aqueous acidic medium under ambient conditions. The solid reagents were prepared from the intermediate obtained in the cold process of bromine manufacture and are stable, nonhazardous and inexpensive to prepare.

This procedure provides an efficient and practical alternative to conventional procedures using liquid bromine directly or indirectly.