CHAPTER I

Introduction to Montmorillonite K-10 and Iodobenzenediacetate

Section A: Montmorillonite Clay

Section B: Iodobenzenediacetate
Chapter I

Section A : Montmorillonite Clay

Points to be studied :

1] Concept of Green Chemistry.

2] Parameters of Green Chemistry.


   7.1 Addition Reaction
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   7.3 Rearrangements
   7.4 Aromatic Electrophilic Substitution
   7.5 Oxidation Reaction
   7.6 Cyclization Reaction

8] References
1] Concept of Green Chemistry:

The desire to make chemical manufacturing environmentally friendly is not a new one. Over the centuries, chemists have been trying to understand and develop chemical processes based on the philosophies that are nature's very own. While working on any synthesis, nature adopts methods following routes that eliminate almost completely the use and generation of substances hazardous to human health and the environment. On the other hand, chemists and technologists do not seem to rank the environment very high in the priorities. This is the reason why natural processes are 'GREEN' while synthetic processes are often 'GREY'.

"By definition, Green Chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use of substances hazardous to human health and the environment."1

Recently, many researchers are working in this relatively new field and trying to reduce the hazardous consequences of the chemical industries. The economic progress and the environmental growth should proceed hand in hand with harmony. In fact, substantial damage to the environment seems to have resulted from the actions of chemists and chemical technologists in the 20th century.2

Consequently there have been efforts to achieve environmentally benign synthesis and the modification of several engineering practices. Number of legislation have been passed for advocating the development of novel technologies and processes with ecofriendly behavior. This revolution is rather recent and started in the real sense in the 1990s, especially in the developed nations like US, UK and Germany.
2] Parameters of Green Chemistry:

An execution of a green chemical reaction or chemical process is to be best done in terms of twelve principles that have been advocated by J. C. Warner. This principles deal with fundamental issues such as pollution prevention, atom economization and toxicity reduction. The essence of twelve principles may be summarized as follows:


ii] Concept of atom economy leading to almost zero waste.

iii] Design of environmentally friendly synthetic methodologies.

iv] Replacing hazardous or expensive reactants and reagents by safer and economical ones.

v] Redundancy of auxiliary substances.

vi] Catalytic reactions instead of stoichiometric ones.

vii] Conservation of energy.

viii] Developing solvent free processes or minimizing the use of solvent or using solvent that can be quantitatively recovered at low cost.

ix] Formulating more efficient isolation and purification procedures.

x] Use of renewable feedstock.

xi] Debasement of final products after the end of their function.

xii] Real-time analysis for pollution prevention.
In achieving many goals of Green Chemistry, catalysts help the synthetic chemist in a big way. An important family of catalysts that has received considerable attention of the synthetic chemist in recent times is derived from the soil, the most noteworthy ones being clays and zeolites. Using clay catalysts, environmentally benign green chemistry can be done both at industrial level and laboratory scale. The catalytic properties of clay can be greatly manipulated to suit the needs of synthetic organic chemists.

Clays are a class of soil with particle size of less than 2 mm in diameter. Their characteristic physical features are, they are sticky and plastic when moist, but hard and cohesive when dry. Structurally, they are crystalline hydrous aluminosilicates, and also contain various other cations.

Clay minerals are made up of layered silicates. There are two basic building blocks viz. tetrahedral and octahedral layers, which are common to clay minerals.

Tetrahedral layers consist of continuous sheets of silica tetrahedra linked via three corners to form a hexagonal mesh. The fourth corner of each tetrahedron (normal to the plane of the sheets) is shared with octahedra in adjacent layers.

Octahedral layers in clay mineral, on the other hand, consist of flat layers of edge-sharing octahedra. Each octahedra formally contains cations such as Al$^{3+}$ or Mg$^{2+}$ at its center and OH$^{-}$ or O$^{2-}$ at its apices. Octahedral layers may be trioctahedral or dioctahedral depending on the degree of occupancy of the octahedral sites.
Depending on the different arrangement of tetrahedral and octahedral layers, clay minerals are classified in the groups such as kaolinite, smectite, illite and vermiculite.

The kaolinite group of clay minerals consist of alternating arrangement of tetrahedral or octahedral sheets (OT or 1:1 structure). The smectite group comprises a sandwich of one octahedral sheet between two tetrahedral sheets (TOT or 2:1 structure).

5] The Structure and Properties of Montmorillonite Clay:

Montmorillonite is the most important and common member of smectite clay groups of minerals.

The Montmorillonite lattice is composed of a octahedrally coordinated gibbsite \([\text{Al}_2(\text{OH})_6]\) sandwiched between two sheets of tetrahedrally coordinated silicate \([\text{SiO}_4]^{4-}\) sheets. The three-sheet layer repeats itself and the interlayer space holds the key to the chemical and physical properties of the clay.

The useful catalytic properties of Montmorillonite originates from its high efficiency for \(\text{M}^+\) cation exchange. This happens because of charge imbalances in its structure caused by exchange of \(\text{Al}^{3+}\) for \(\text{Si}^{4+}\) in the
tetrahedral sheets, and of Mg\(^{2+}\) for Al\(^{3+}\) cations in the octahedral sheets. The defects at the edges of crystals also add to this imbalance. The imbalance of charge due to isomorphous substitution is compensated by the cations presumably situated between the lattice layers. On wetting, the layers move apart by the entry of water molecules, thereby the clay swells and the existing interlayer cations become easily exchangeable.

The interlayer in Montmorillonite clay normally contains Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) as compensatory cations for the charge imbalance. When the clay is dry, these cations reside in the hexagonal cavities of the silica sheets. However, when it is treated with water, the cations relocate themselves in the interlamellar region and become exchangeable by a variety of both metallic and nonmetallic cations, for example, H\(_3\)O\(^+\), NH\(_4\)^{+}, Al\(^{3+}\), Fe\(^{3+}\), Rb\(^+\), P\(_4\)P\(^{3+}\) etc. One of the most useful properties of clay minerals lies in this fact.

6] **Acidic Character of Clay** :

A variety of organic reactions that are catalyzed by Bronsted acids such as H\(_2\)SO\(_4\), HCl, HNO\(_3\), AcOH etc. or Lewis acids such as AlCl\(_3\), TiCl\(_4\), FeCl\(_3\), etc. have been shown to take place in clays, especially montmorillonite, more efficiently, i.e. under milder conditions, with greater selectively, better yields, shorter reaction times and so on. Moreover, the work up and purification procedure are simpler as the catalyst is separated easily from the reaction mixture by mere filtration. Because of these reasons, and the fact that the catalyst can be reused or regenerated, the entire synthesis activity is not only economical but also environmentally benign.9

Clays possess both the Lewis and the Bronsted acidity. The Lewis acidity is due to Al\(^{3+}\) and Fe\(^{3+}\) at the crystal edges and can further enhanced by exchange of the interlayer cations Na\(^+\) and Ca\(^{2+}\) by Al\(^{3+}\) ions on treating the clay with AlCl\(_3\) solution.
The Bronsted acid character of clays arises due to the dissociation of the intercalated water molecules coordinated to cations (equation 1).\textsuperscript{10} Higher levels of Bronsted acidity are achieved when highly polarizing ions such as Cr\textsuperscript{3+} have exchanged for Na\textsuperscript{+}, Ca\textsuperscript{2+}, etc. present in the natural clay, and the other content is low.

\[
[M(H_2O)_n]^{3+} \leftrightarrow [M(H_2O)_{n-1}OH]^{2+} + H^+ \quad (1)
\]

Besides the total acidity, the surface area and the pore volume in the clay structures also add to the efficiency of the catalyst. Total acidity can be further increased by 'proton-exchange' on treating the clay with dilute acid or driving out NH\textsubscript{3} by heating NH\textsubscript{4}\textsuperscript{+} ions treated clay. P. Laszlo, a pioneer of clay catalysis, has proved that Montmorillonite have surface acidities that place them between concentrated nitric and sulfuric acids. It is clear from this description that strong corrosive acid medium is completely avoided, if we use clay as Bronsted acid instead of mineral acids to achieve the same purpose.

7] Organic Reactions in Clay Media :

The range of reactions that have been successfully performed on clay catalysts includes addition, elimination, addition-elimination, substitution, rearrangement, Diels-Alder reactions, oxidation-reduction reaction and others. It is not possible to give many examples, but an attempt is made to give a few representative reactions for gaining some insight into this area of organic synthesis.

7.1] Addition Reactions :

Acid-treated and various cation exchanged Montmorillonite clays are effective catalysts for a wide variety of addition reactions.\textsuperscript{11} Both Bronsted and Lewis acidity play a role in the catalytic activity. Treatment of clays with acids creates Bronsted acid sites.
Alcohols can add to alkenes in the presence of Montmorillonite to afford ethers.\textsuperscript{12-13} The reaction with 1-alkenes, however, is slow and results in a mixture of alk-2-yl and alk-3-yl ethers.

\[
\begin{align*}
RCH_2CH\equiv CH_2 & \xrightarrow{H^+ - \text{Mont.}} RCH_2CHCH_3^+ \\
& \xrightarrow{i) R^1 XH \text{ (alk-2-yl)}} \xrightarrow{ii) - H^+} RCH_2CHCHR^1 \\
& \text{where } X = S, O, OCO
\end{align*}
\]

Hydrogen sulfide and thiols add to alkenes in the presence of acid-treated and Al(III) exchanged Montmorillonite at 200 °C to provide dialkyl sulfides in good yields.\textsuperscript{14}

\[
RCH=CH_2 + R' \text{SH} \xrightarrow{\text{Al(III) Mont.}} \xrightarrow{200 \degree C} RCHCH_3SR^1
\]

The addition of carboxylic acids to alkenes takes place over Al(III)- exchanged or proton-exchanged Montmorillonite to provide esters.\textsuperscript{15}

7.2] Elimination Reactions:

One of the most widely investigated field of clay-catalyzed processes is the dehydration of alcohols. The product (alkene and/or ether) depends on the catalyst used.

The intramolecular dehydration of alcohols is efficiently catalyzed by both Al(III) as well as H\textsuperscript{+} exchanged clays.\textsuperscript{16}

Primary alcohols afford mainly dialkyl ethers with little alkene production whereas secondary and tertiary alcohols provide alkenes exclusively.
\[
\begin{align*}
\text{RCH}_2\text{CH}_2\text{OH} & \xrightarrow{100 \degree C} \text{Al (III)-Mont.} \quad \text{RCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{R} + \text{RCH}=\text{CH}_2 \\
\end{align*}
\]

For example, cyclohexanol undergoes easy dehydration to give high yields of cyclohexene accompanied by little amount of dicyclohexyl ether.\(^{17}\)

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{Al (III)-Mont.} \\ 200 \degree C} \text{cyclohexene} + \text{dicyclohexyl ether} \\
\end{align*}
\]

\[
\begin{array}{c}
\text{88 \%} \\
\text{4 \%}
\end{array}
\]

7.3) **Rearrangements:**

Many rearrangements are mediated by carbocations and thus are triggered by the use of acidic conditions. Accordingly, acidic and ion-exchanged clays or clay supported reagents provide convenient and efficient catalysts for rearrangements.

\(\text{Al}^{3+}\) ion-exchanged Montmorillonite are effective in the Fries rearrangement.\(^{18}\) Phenyl benzoate, for instance, is converted into 2-hydroxy benzophenone.\(^{19}\)

\[
\begin{align*}
\text{PhO} & \xrightarrow{\text{Al}^{3+}\text{-Mont.} \\ 180 \degree C, 4h.} \text{2-hydroxy benzophenone} \\
\end{align*}
\]

49 \% Yield

Cation exchanged Montmorillonites are used as effective catalysts for the facile rearrangement of phenyl toluene-para-sulfonate to give 2-and 4-hydroxyphenyl-4-tolylsulfones.\(^{20}\) Selectively for the ortho-isomer can be as high as 93 \% (\(\text{Cu}^{2+}\) - Montmorillonite) and as low as 65 \% (\(H^+\) - Montmorillonite). Bosch et al. have accomplished the Beckmann rearrangement of ketoximes with Montmorillonite K-10 clay in 'dry' media in good yields.\(^{21}\)
7.4) Aromatic Electrophilic Substitution (Friedel-Crafts Reaction):

There are numerous disadvantages in using stoichiometric amounts of AlCl₃ in the industrially significant Friedel-Crafts reaction that are associated with pollution load on the environment. Montmorillonite supported transition metals salts (zinc and nickel chlorides) are highly active and selective reagents for the catalysis of Friedel-Crafts alkylation and circumvents some of the drawbacks.²²-²³

The Friedel-Crafts acylation of anisole, mesitylene and xylene by Fe(III) modified clay provides good to quantitative yields of the derivatives.²⁴

Montmorillonite supported cupric nitrite has been used in the regioselective nitration of aromatic hydrocarbons.²⁵ A vastly increased para-preference is reported in the nitration of halobenzenes.²⁶

The acid treated Montmorillonite has been used to catalyze the electrophilic substitution of protonated formaldehyde to aromatic amines and phenols to produce diaryl methane derivatives of commercial interest.²⁷
7.5] Oxidation Reactions:

There are several oxidation reactions in which the clays are either the catalysts or the inorganic supports. Supported oxidizing reagents are species with controlled reactivity which offers distinct advantages over the reactions carried out under homogeneous conditions. Separation of excess reagent and isolation of the products require only simple filtration and evaporation of the solvent.

Clayfen and Claycop as Versatile Oxidizing Agents:

Impregnation of Fe(III) and Cu(II) nitrates onto Montmorillonite K-10 produced a novel class of multipurpose reagents termed clayfen and claycop, respectively by Laszlo and co-workers.\textsuperscript{28-29}

Clayfen is utilized as an efficient catalyst in several oxidation reaction. For example:

- Oxidation of alcohols\textsuperscript{28} (~90 % yield of aldehydes without over-oxidation to carboxylic acids in the case of primary alcohols).
- Oxidation of benzoin to benzil.\textsuperscript{30}
- Oxidation, coupling of thiols to disulfides.\textsuperscript{31}
- Regeneration of carbonyls from their various protected forms such as tosylhydrazones, phenylhydrazones and semicarbazones.\textsuperscript{32}

7.6] Cyclization Reactions:

Ring closure reactions can be promoted by clays or clay supported reagents. Some of them require high temperature while the others are mild, selective and convenient procedure of significant preparative value.
A convenient one-pot synthesis of 2,3-distributed-indoles has been performed from phenylhydrazine and ketones using Montmorillonite clay as catalyst.\textsuperscript{33}

\[
\text{NHNNH}_2 + R^1\text{COCH}_2R^2 \overset{\text{Mont.}}{\longrightarrow} \text{\begin{tikzpicture} \node[anchor = north] at (0,0) {\text{\textcolor{blue}{N}}\text{H}\text{\textcolor{red}{R}}^1\text{R}^2}; \end{tikzpicture}}
\]

Montmorillonite K-10 clay under microwave irradiation conditions enables solvent free cyclization reaction wherein readily available 2-amino-chalcones provide easy access to 2-aryl-1,2,3,4-tetraydro-4-aminoquinolones.\textsuperscript{34}

\[
\text{\begin{tikzpicture} \node[anchor = north] at (0,0) {\text{\textcolor{blue}{N}}\text{H}\text{\textcolor{red}{Cl}}\text{MeO}}; \end{tikzpicture}} + \text{\begin{tikzpicture} \node[anchor = north] at (0,0) {\text{\textcolor{blue}{N}}\text{H}\text{\textcolor{red}{Cl}}\text{MeO}}; \end{tikzpicture}} \overset{\text{Mont. K-10, MW, 1-2 min.}}{\longrightarrow} \text{\begin{tikzpicture} \node[anchor = north] at (0,0) {\text{\textcolor{blue}{N}}\text{H}\text{\textcolor{red}{Cl}}\text{MeO}}; \end{tikzpicture}}
\]
References:


   


Chapter I

SECTION B : Iodobenzenediacetate : A Versatile Hypervalent Iodine Reagent

Points to be Studied:

1] Introduction
2] Examples and Classification
3] Need to Study Hypervalent Iodine Reagents
4] Bonding and Structure in Hypervalent Iodine
5] Practical Aspects
6] Preparative Methods for Hypervalent Iodine Reagents
7] Reactivity Pattern
8] References
1] Introduction:

Iodine was discovered in 1811. Although it is relatively uncommon in nature, it plays an important role in biological organisms, including humans, for whom it is essential for the proper functioning of the thyroid gland.

Iodine is found most often as monovalent compounds and forms relatively weak bonds with first-row elements including carbon. However, because it is the most polarizable and largest element among the common halogens, it is also capable of forming stable polycoordinate, multivalent compounds.

“Organic compounds of iodine with coordination number more than one are known as hypervalent iodine compounds”.

Just over a hundred years ago, in 1885, the German Chemist C. Willgerodt reported the preparation of first organic compound of polyvalent iodine – (dichloroiodo)benzene, PhICl₂.¹ From 1885 to 1980, the progress in hypervalent iodine compounds was relatively slow with the notable discovery of diacetoxyiodobenzene² and diaryliodonium bisulfate.³ From 1980 to 1992, an explosive growth occurred in the field of hypervalent iodine in organic synthesis. More than a dozen individual compounds have currently reached the status of reagent, and numerous members from various classes have emerged as valuable synthetic intermediates. This is witnessed by more than 30 reviews published on hypervalent iodine in organic synthesis during 1990 to 2001.⁴⁻³⁶

The chemistry of hypervalent iodine compounds includes a wealth of important, sometimes unique, reactions, offering powerful synthetic tools. Today their exclusion from the arsenal of the organic chemist is inexcusable.

2] Examples and Classification:

Several classes of hypervalent iodine compounds are known – some with few and some with many members.³⁷ The large numbers of compounds
contain iodine attached to 2-4 widely differing ligands. Most reagents can be readily obtained by established procedures. A dozen of hypervalent iodine reagents are already commercially available. In fact, some are presently well known, especially (diacetoxyiodo)benzene, Kosser’s and Dess-Martin reagents.39

The most important reagents can be divided in two broad categories: individual compounds and classes, these most frequently used are illustrated in Table 1.

Table 1: The commonest reagents of hypervalent iodine

<table>
<thead>
<tr>
<th>a. Individual Compounds</th>
<th>Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dichloroiodo)benzene</td>
<td>PhICl₂</td>
<td>-</td>
</tr>
<tr>
<td>(Diacetoxyiodo)benzene</td>
<td>PhI(OAc)₂</td>
<td>DIB</td>
</tr>
<tr>
<td>[Bis(trifluoroacetoxy)iodo]benzene</td>
<td>PhI(O₂CCF₃)₂</td>
<td>BTI</td>
</tr>
<tr>
<td>Iodosylbenzene</td>
<td>PhIO</td>
<td>IOB</td>
</tr>
<tr>
<td>[(Hydroxy)(tosyloxy)iodo]benzene</td>
<td>PhI(OH)OTs</td>
<td>HTI</td>
</tr>
<tr>
<td>Iodylbenzene</td>
<td>PhIO₂</td>
<td>-</td>
</tr>
<tr>
<td>Dess-Martin reagent</td>
<td><img src="image" alt="DM" /></td>
<td>DM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b. Classes</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diaryliodonium salts</td>
<td>Ar₂I⁻X⁻</td>
</tr>
<tr>
<td>Vinyl phenyl iodonium salts</td>
<td>PhI⁺CH=CHR X⁻</td>
</tr>
<tr>
<td>Alkynyl phenyl iodonium salts</td>
<td>PhI⁺C=CR X⁻</td>
</tr>
<tr>
<td>Perfluoroalkyl phenyl iodonium salts</td>
<td>PhI⁺Rf X⁻</td>
</tr>
<tr>
<td>Iodonium ylides and dipoles</td>
<td>Diverse formulas</td>
</tr>
</tbody>
</table>
3] Need to study Hypervalent Iodine Reagents:

Promotion of the use of Hypervalent iodine reagents is desirable for a number of reasons:

1. They are environmentally benign and can be recycled. Also they replace heavy metal oxidants [Hg(II), Tl(III) and Pb(IV)], a property particularly welcome by the pharmaceutical industry. Their wider use will mean significantly more Green Chemistry.\textsuperscript{30}

2. Compounds with I\textsuperscript{III} and other polyvalent main group and transition metal coordination compounds are very similar in chemical behavior w. r. t. certain catalytic fundamental processes like ligand exchange, reductive elimination, etc.\textsuperscript{40}

3. This often brings about unique transformations, not possible by other reagents.

4. They have operational simplicity, under mild reaction conditions, avoiding the use of excessive energy.

5. They have great potential for further elaboration by changing 1-5 ligands of great structural variety attached to iodine.

6. In addition to their synthetic utility, several hypervalent iodine compounds have found applications in biomedical research and in industrial processes. Therefore an acquaintance with them should be beneficial.

4] Bonding and Structure in Hypervalent Iodine:

Organic compounds of poly-co-ordinated iodine, called as iodonens, comprises several classes in which iodine has a coordination number from 2 to 5. From a practical point of view, the great majority of useful compounds are derived from iodobenzenes, in which iodine is linked to 1-4 electronegative
ligands such as halogen (F or Cl), OH, OR, RCOO, RSO₃ etc. Some members of this family are actually ionic and may be written either as iodonium salt, PhI⁺LL⁻, or with the convention PhILL, their true nature in solution depends on the solvent.⁴¹

The term hypervalent refers to bonding in elements of Groups V-VII of the periodic table. It is applied when these elements contain 10 or 12 electrons in their outermost shell. In other words such elements have valence higher than the normal.

In iodanes of the IL₃ type the less electronegative phenyl ring is bound to iodine by a normal covalent bond. It lies in the equatorial position of a trigonal bipyramid. The other two ligands are at the axial positions, attached, one to each lobe, to one doubly occupied sp-orbital of iodine. This arrangement results in a linear three-centre four electron (3c-4e) bond system. In this way a single orbital of iodine participates to two 3c-4e bonds, usually called hypervalent; these are longer and weaker than the covalent bond. The molecule adopts a T-shaped structure. This is justified by the following electronic formula for a typical member, (dichloroiodo)benzene.

![Figure 1: The electronic structure of (dichloroiodo)benzene](image_url)
5] Practical Aspects:

1. All hypervalent iodine reagents are solids – amorphous or crystalline – colourless and odorless.

2. They are fairly stable to room temperature.

3. Insensitive to atmospheric oxygen and moisture.

4. Upon storage, the light protection and refrigeration is recommended.

5. Easy handling, e.g. PhICl$_2$ for chlorination reaction can be weighed accurately for maintaining the requisite stoichiometry.$^{42}$

6. Operationally simple reactions - the reactions are usually performed in non-complicated apparatus, often in open vessels.

7. Most of the reactions are at room temperature with quite shorter reaction time.

8. After reaction, work-up procedures normally involve chromatographic separation, especially when iodobenzene is the main by-product. This drawback is offset by the possibility of collecting and recycling this relatively expensive starting material.

On the other hand, iodobenzene can be disposed of without problems, since it is environmentally acceptable because of its low toxicity and ready biodegradability.$^{37}$

6] Preparative Methods for Hypervalent Iodine Reagents:

Most hypervalent iodine reagents are obtained from readily available starting material namely iodobenzene. Their preparation does not involve dangerous, demanding or time consuming methods. Some reagents are commercially available.$^{43}$
• Preparation does not involve dangerous, demanding or time consuming protocol.

• Ample availability of starting material.

• Commercial availability of few reagents.\textsuperscript{44}

7) Reactivity Pattern:

The rich chemistry of hypervalent iodine is primarily due to two important factors:\textsuperscript{37}

i) Strong Electrophilic Character of Iodine:

Iodine in both $\lambda^3$ – and $\lambda^5$ – iodanes is a good soft electrophilic centre which can be attacked by virtually any nucleophile. As a result, new iodine species of varying stability are formed upon reaction with substrates.

\[
\text{PhIL}_2 \xrightarrow{\text{Nu}} \text{[PhIL}_2\text{Nu]}^+ \xrightarrow{\text{-L}} \text{PhILNu}
\]
The intermediate 2, which can be isolated in some cases is transformed into new iodane 3 with the ligand dissociation process.

ii) Superleaving Group Ability of the Phenyliodonio Group:

The weak hypervalent bonds in intermediates 2 or 3 are readily broken, resulting in reductive elimination of iodobenzene and formation of the end-products.

\[
\begin{align*}
2 & \quad \text{OR} \quad 3 \quad \xrightarrow{\text{reductive elimination}} \quad \text{L} - \text{Nu} + \quad \text{PhI} \\
\text{product} & \quad \text{can be recycled}
\end{align*}
\]

This tendency to expel iodobenzene converts the initial electron-rich substrates into electron deficient species through umpolung for nucleophilic counterpart. This leads to many useful transformations.

The above discussed reactivity pattern of a hypervalent iodine reagents, PhIL₂ can be justified by the following magical transformation.

\[
\text{Ph} - \text{CO} - \text{OH} \quad \xrightarrow{?} \quad \text{Ph} - \text{CO} - \text{CO}
\]

In this one step transformation, it is very difficult to form a bond in one step between α-carbon to keto group and nucleophilic –OH of carboxylic group because both sites are potentially nucleophilic in nature. But, a hypervalent ionide reagent like PhI(OH)OTs can bring about this reaction very much magically.⁴⁵

\[
\text{Ph} - \text{CO} - \text{CO} - \text{OH} \quad \xrightarrow{\text{PhI(OH)OTs}} \quad \text{CH₂Cl₂, reflux} \quad \text{74%}
\]

Mechanistically, the reaction proceeds through the following reaction sequence.
The mechanistic steps like ligand association through nucleophilic attack on electrophilic iodine, ligand dissociation, the versatile tendency of iodine for assembling the reactive ligands and finally the reductive elimination of iodobenzene can easily justify the unique reactivity pattern of hypervalent iodine reagents.

This reactivity pattern of hypervalent iodine reagents is very much parallel to heavy metal analogous like Hg(II), Tl(III) and Pb(IV), but without the toxic and concomitant environmental problems.
### References and Some Reviews about Hypervalent Iodine


