Section B

“A Simple protocol for Oxidative decarboxylation using oxone and Iodobenzene”


**Part B: Using Reagents like Oxone and Iodobenzene:**

**Abstract**

This is facile and novel protocol for the oxidative decarboxylation of phenyl acetic acid and $\alpha$-substituted phenyl acetic acid by active hypervalent Iodine (III) species generated in situ, from Iodobenzene and Oxone as a highly active reaction system was developed. The generated species exhibited remarkable activity and also used in oxidative decarboxylation of $\alpha$-substituted phenyl acetic acid to obtainable product in good yield. The protocol was applicable for a variety functionalized phenyl acetic acid and afforded the desired benzaldehydes, ketones as products in good to excellent yield. Advantages of this system are short reaction time, easy work-up and good yields.

**Scheme 2B.1**

![Scheme 2B.1](image)

**2B.1 Introduction**

Viktor V. Zhdankin et al found that active iodine (III) species [i.e. (hydroxy (phenyl) iodonium ion)] can be inventively generated in solution by treatment of Iodobenzene with oxone in aqueous acetonitrile at room temperature.

Oxone and Iodobenzene reaction system is better reagent for this transformation and shows amino group oxidation properties. This reaction was carried out in Acetonitrile/water reaction system which is helpful for further hydrolysis of imine which is formed in reaction for preparation of aldehyde as major product. We have used this combination to present methodology. We became successful in
formation of desired product in good yields which will be studied in this chapter in detail.

![Scheme 2B.2](image)

2B.2 Literature Survey:

We already discussed in our previous chapter that Oxidative decarboxylation of phenyl acetic acids and α-substituted phenyl acetic acids are very important transformation in organic synthesis, also we studied about oxidative decarboxylation regarding phenyl glycine that formed nitrile.

The present transformation explain about oxidative application of hypervalent active (III) species generated in situ from Oxone and Iodobenzene in aqueous acetonitrile solvent system for the transformation of phenyl acetic acid and α-substituted phenyl acetic acid to their corresponding products. We also notified that when phenyl glycine was subjected to this transformation we got aldehyde as major product.

2B.3 Objectives and Scope

Expansion of new method for the oxidation of phenyl acetic acid and α-substituted phenyl acetic acids to corresponding products using hypervalent iodine (III) Species generated in situ from Iodobenzene and inexpensive commercial oxidant Oxone (2KHSO₅•KHSO₄•K₂SO₄) was conceived (Scheme 2B.1) Projected innovative route for synthesis of substituted benzaldehydes and ketones was carried out using respective phenyl acetic acid and α-substituted phenyl acetic acid as starting material. The key reaction was Generation of Active Iodine (III) Species from Iodobenzene and Oxone in aqueous acetonitrile solvent at room temperature. This is responsible for Oxidative decarboxylation of starting material to particular product.
2B.4 Work done on each objective:

Flexible applicability of benzaldehydes, ketones moiety and drawbacks of literature methods for its synthesis led us to develop innovative route for its synthesis. Other view of developing new methodology was the disadvantages of the available literature methods which includes either highly acidic condition, unwanted oxidations, side reactions and long reaction times.

In case of oxidative degradation of α-amino acids by using coenzyme PQQ/cetyltrimethyammonium bromide many of these reports on the oxidative decarboxylation of α-amino acid have drawbacks like low amount of yield, mostly aliphatic acids under goes this transformation, longer reaction time and lower substrate compatibility, which limits their applications. Recently, in our lab oxidative decarboxylation of phenyl acetic acid, α-alkyl or aryl phenyl acetic acid and α-amino acids to respective products using DIB/NaN₃ in acetonitrile solvent has been developed (Telvekar et al., 2010). In case of α-amino acid we got nitrile as product with good yield reaction carry out at room temperature, in our methodology there are also some limitations that use of sodium azide.

![Scheme 2B.3](image)

Therefore there is scope for development of novel route for oxidative decarboxylation of phenyl acetic acid, α-alkyl or aryl phenyl acetic acid, mendalic acid and α-amino phenyl acetic acid to their resultant product to overcome some of these drawbacks.

Viktor V. Zhdankin and co-workers have recently found that active iodine (III) species [i.e., (hydroxy (phenyl) iodonium ion, 1] can be powerfully generated in solution by simple treatment of Iodobenzene with Oxone in aqueous acetonitrile at

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\[ \text{Scheme 2B.3} \]

\[ \text{Where } R = \text{H, OH, alkyl, aryl etc} \]

\[ \text{Or } R = \text{H, OH} \]

\[ \text{R = alkyl, aryl etc} \]
room temperature (Scheme 2B.4). This generated Species (1) is recently found very important in organic transformations there are so many examples in which this Combination of Oxone and Iodobenzene is used to develop variety of transformations (Yusubov et al., 2009; Zhdankin et al., 2009; 2010).

![Scheme 2B.4](image)

The successful functioning of Oxone/Iodobenzene combination in development of one carbon dehomologation reactions (Scheme 2B.4)

**2B.5 Mechanism of Oxone and Iodobenzene:**

![Fig 2B.1](image)

A reaction mechanism involving the formation of $\lambda^5$- and $\lambda^3$-iodanes as active hypervalent reagents has been projected, some examples of Iodobenzene and Oxone Reagent reaction system (Fig 2B.1).
With these reactions as background, herein we determined the expansion of this chemistry. We subjected phenyl acetic acid to react with Oxone and Iodobenzene combination to obtained benzaldehyde as product through Oxidative decarboxylation phenomenon as shown in (Scheme 2B.5)
We found that for synthesis of ketones from α- alkyl or aryl phenyl acetic acid there is requirement of catalytic amount of KBr for increase of amount of yields, in absence of KBr reaction gives very low yield (Scheme 2B.6)

\[
\text{Oxone / Iodobenzene} \quad \text{Cat. KBr,aq. Acetonitrile} \quad \text{r.t}
\]

where R = alkyl, aryl etc.

Scheme 2B.6

2B.6 Results and Discussion

To develop a suitable protocol for oxidative decarboxylation reaction initially the phenyl acetic acid treated with Oxone (2 mmol) and Iodobenzene (2 mmol) in the acetonitrile water solvent system at room temperature was chosen as a model reaction as expected benzaldehyde was obtained in exceptional yields in 45 min. Completion of the reaction was monitored by Thin Layer Chromatography (TLC). After completion of reaction, workup carried out as given in experimental procedure, pure product was isolated by column chromatography.

Product obtained was characterized with the physical and spectral properties and compared with authentic sample. It was confirmed that benzaldehyde is the product.

**Benzaldehyde** (Entry1): Liquid, BP 177 °C IR (KBr): 2821, 2734, 1704,1597,1430,1361 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta=10.00\) (1H, s), 7.87 (2H, d, \(J = 7.0\)), 7.62 (1H, t, \(J = 7.3\)), 7.52(2H, t, \(J = 7.2\)).
To expand the scope of our reaction system \( \alpha \)-hydroxyl and \( \alpha \)-amino phenyl acetic acid subjected to oxidative decarboxylation, in both cases we were found to respond smoothly providing highest yield of benzaldehyde as preferred product. It is noteworthy to mention that no Benzonitrile product in case of phenyl glycine was obtained.

To explore the simplification and applicability of the protocol, we turned our attention towards the oxidative decarboxylation of \( \alpha \)-alkyl phenyl acetic and \( \alpha \)-aryl phenyl acetic acid with oxone (2mmol), Iodobenzene (1mmol) and catalytic KBr providing good to excellent yields of the desired product. We also checked the role catalytic KBr in Our reaction System In the presence of KBr the yield of the desired product was finest, that is 82\% however, in the absence of KBr the yield obtained fair.

\[
\text{\[\text{CH}_3\]}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 2.5 (3H, s), 7.56-7.96(5H, m), IR (FTIR) 1690, 1599, 1450, 1267, 691, 1603 cm\(^{-1}\)

To begin systematic study for the conversion we have chosen phenyl acetic acid as model substrate to optimize reaction conditions and substrate study for the simplification of transformation with chemoselectivity.

a. Solvent study

b. Temperature and reaction time

c. Reagent mole ratio

d. Generality of the substrates
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a. Solvent study

After successful formation of benzonitrile as product, various types of solvent study were done and result summarised in (Table 2B.1)

Table 2B.1: Influence of Solvent.

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Solvent</th>
<th>Substrate (mmol)</th>
<th>Temp.</th>
<th>Time(min)</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MDC</td>
<td>1</td>
<td>R.T</td>
<td>45</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>Acetone:H₂O</td>
<td>1</td>
<td>R.T</td>
<td>45</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>CH₃CN:H₂O</td>
<td>1</td>
<td>R.T</td>
<td>45</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>CH₃CN</td>
<td>1</td>
<td>R.T</td>
<td>45</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>Water</td>
<td>1</td>
<td>R.T</td>
<td>45</td>
<td>72</td>
</tr>
</tbody>
</table>

It was observed that the reaction given Good results with the use of acetonitrile and Water Solvent System.

b. Temperature and reaction time

Optimization of reaction condition in terms of time and temperature is also carried out and results are shown in (Table 2B.1). Reactions were carried out at different temperatures from room temperature to reflux and it was observed that reactions are clean, smooth and gives better yields at room temperature. In case of phenyl acetic acid reaction was finished in 45 min. and no further change was observed even after continuing the reaction for 24 h. However in case of α-aryl or alkyl phenyl acetic acid, reaction requires more than 2 h for completion of reaction.

c. Reagent Mole Ratio

1. Oxidative decarboxylation of phenyl acetic acid and α- hydroxy or α- amino phenyl acetic acid.
Experiments were carried out using varied mmol of Oxone and Iodobenzene. Initially, the reaction was carried out by using 0.5 mmol of oxone and Iodobenzene (2mmol), which provided desired product in 40% yields. An increase in the oxone concentration up to 2 mmol resulted in an increase in the yield of 86% (Table 2B.2, Entry 4). Further increase in the amount of oxone had no profound effect on the yield of the desired product (Table 2B.2, entry 5).

Also, the reaction was carried out at different Iodobenzene concentration ranging from 0.5 mmol 2 mmol (Table 2B.3, entries 5-9). It was observed that when Iodobenzene concentration is 0.5mmol then the yield of the product was very low(Table 2B.3, entry 6) and with an increase up to 2 mmol, the yield of product increased to 86%(Table 2B.3, Entry 9) However, a further increase in concentration did not show any significant enhancement in the yield (Table 2B.3, entry 10).

**Table 2B.2 Effect of Reagent Concentration:**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Oxone(2mmol)</th>
<th>Iodobenzene(2mmol)</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>2</td>
<td>86</td>
</tr>
</tbody>
</table>

![Scheme 2B.7](image-url)
Table 2B.3 Effect of Iodobenzene Concentration:

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Oxone (2mmol)</th>
<th>Iodobenzene (2mmol)</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>0.5</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
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</tr>
<tr>
<td>8</td>
<td>2</td>
<td>1.5</td>
<td>74</td>
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<tr>
<td>9</td>
<td>2</td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>2.5</td>
<td>86</td>
</tr>
</tbody>
</table>

Oxidative decarboxylation of $\alpha$-alkyl phenyl acetic or $\alpha$-aryl phenyl acetic acid with oxone (2mmol) and Iodobenzene (1mmol) (Table 2B.4, entry 1) the reaction gave 45% yields of ketones, we also checked the role KBr in Our reaction System In the presence of Catalytic KBr, the yield of the desired product was finest that is 82% however, in the absence of KBr the yield obtained fair. Further increase in Iodobenzene or oxone concentration did not show any significant enhancement in the yield.

Table 2B.4 Effect of Iodobenzene Concentration in case of Oxidative decarboxylation of $\alpha$- alkyl or aryl phenyl acetic acid:

\[
\text{Oxone/Iodobenzene(2:1)} \rightarrow \text{Oxone/Iodobenzene(2:1)}
\]

Where R=alkyl,aryl etc

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Oxone (2mmol)</th>
<th>Iodobenzene (mmol)</th>
<th>Cat.Kbr (0.05mmol)</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>✓</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>✓</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1.5</td>
<td>✓</td>
<td>78</td>
</tr>
</tbody>
</table>
2B.6.1 Optimized Reaction Condition

1. Synthesis of benzaldehydes:

With these studies, it is noted that best results were obtained with 2 mmol of Oxone and 2 mmol Iodobenzene in aqueous acetonitrile at room temperature and all further reactions were carried out using these optimized parameters.

2. Synthesis of ketones from α-aryl or alkyl phenyl acetic acid:

With these studies, it is noted that best results were obtained with 2 mmol of Oxone and 1 mmol Iodobenzene and catalytic amount of KBr is required in aqueous acetonitrile at room temperature and all further reactions were carried out using these optimized parameters.

d) Generality of the Substrates

With these hopeful results in hand we went to ensure the feature and convenience of the reaction, by performing the reaction on various substrates including simple phenyl acetic acid and also α- substituted phenyl acetic acids and results are summarised in Table 2B.5.

Table 2B.5: Oxidative decarboxylation of aryl carboxylic acids using Oxone and Iodobenzene in aq. Acetonitrile

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Substrate</th>
<th>Product</th>
<th>Time(Min)</th>
<th>Yield%</th>
</tr>
</thead>
</table>
| 1     | \[
\begin{array}{c}
\text{Ph} \\
\text{COOH}
\end{array}
\] | \[
\begin{array}{c}
\text{Ph} \\
\text{CHO}
\end{array}
\] | 40 | 85 |
| 2     | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{Ph} \\
\text{COOH}
\end{array}
\] | \[
\begin{array}{c}
\text{Ph} \\
\text{C}(\text{H}_3)\text{C} \\
\text{CHO}
\end{array}
\] | 45 | 85 |
| 3     | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{Ph} \\
\text{COOH}
\end{array}
\] | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{Ph} \\
\text{COH}
\end{array}
\] | 45 | 85 |
<table>
<thead>
<tr>
<th>No.</th>
<th>Structures</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td><img src="image1.png" alt="Structure 4" /></td>
<td>45-80</td>
</tr>
<tr>
<td>5</td>
<td><img src="image2.png" alt="Structure 5" /></td>
<td>45-75</td>
</tr>
<tr>
<td>6</td>
<td><img src="image3.png" alt="Structure 6" /></td>
<td>50-75</td>
</tr>
<tr>
<td>7</td>
<td><img src="image4.png" alt="Structure 7" /></td>
<td>60-80</td>
</tr>
<tr>
<td>8b</td>
<td><img src="image5.png" alt="Structure 8" /></td>
<td>130-82</td>
</tr>
<tr>
<td>9</td>
<td><img src="image6.png" alt="Structure 9" /></td>
<td>125-80</td>
</tr>
<tr>
<td>10</td>
<td><img src="image7.png" alt="Structure 10" /></td>
<td>135-82</td>
</tr>
<tr>
<td>11</td>
<td><img src="image8.png" alt="Structure 11" /></td>
<td>40-85</td>
</tr>
<tr>
<td>12</td>
<td><img src="image9.png" alt="Structure 12" /></td>
<td>45-90</td>
</tr>
<tr>
<td>13</td>
<td><img src="image10.png" alt="Structure 13" /></td>
<td>45-80</td>
</tr>
</tbody>
</table>
**Part B: Using Reagents like Oxone and Iodobenzene**

Chapter 2

### Novel Synthetic Methodologies for Bioactive Molecules

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**Table 2B.5**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate Structure</th>
<th>Reaction Time</th>
<th>Isolated Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td><img src="image1.png" alt="Substrate Structure" /></td>
<td>50</td>
<td>85</td>
</tr>
<tr>
<td>15</td>
<td><img src="image2.png" alt="Substrate Structure" /></td>
<td>24h</td>
<td>dNR</td>
</tr>
</tbody>
</table>

*a* Reaction conditions: substrate (1 equiv), Oxone (2 equiv), Iodobenzene (2 equiv) in aqueous acetonitrile at room temperature.

*b* Oxone (2mmol), Iodobenzene (1mmol) and Catalytic KBr required (entry 8-10).

*c* Isolated yields by column chromatography and structures were confirmed by comparison of IR and $^1$H NMR with authentic materials.

*d* NR: no reaction.

To explore generality of the reaction variety of substrates were reacted with optimized reaction condition i.e. 2mmol of oxone in combination with Iodobenzene at r.t in aqueous acetonitrile and results are summarized in (Table 2B.5).

In order to study the promising and general applicability of the developed methodology, various phenyl acetic acids containing different functional groups were subjected to this transformation. We observed that electron donating as well as electron withdrawing groups provided significant yield of products. A variety of functional groups including methoxy, methyl, chloro, isopropyl group, were well tolerated and gave good yield (Table 2B.5, entry 2-6). In order to study the $\alpha$-alkyl or aryl phenyl acetic acid under these reaction conditions, we treated $\alpha$-methyl phenyl acetic acid with Oxone and Iodobenzene which was resulted in the formation of poor yield of ketones. So, by increasing Iodobenzene concentration and use of KBr Improving reaction conditions good yields were achieved (Table 2B.5, entry 8, 9, 10).

To expand the scope of our reaction system $\alpha$-hydroxyl and $\alpha$-amino phenyl acetic acid subjected to oxidative decarboxylation in both cases we were found to respond smoothly providing highest yield of products benzaldehyde as preferred product (Table 2B.5, entries 12-14) it is noteworthy to mention that no Benzonitrile product in case of phenyl Glycine was obtained.

However, no reaction was observed when aliphatic acids were subjected under this reaction conditions (Table 2B.5, entry 15). All formed products were...
characterized by comparing spectral properties and comparing their physical properties with that of reported compounds in the literature. Detail data is presented in the experimental section. All aldehydes and ketones showed characteristic C=O and C-H bond stretching peak.

\[ ^{1}{\text{HNMR of 4-isopropylbenzaldehyde (Table 5, Entry 3)}} \]
IR Spectra of 4-isopropylbenzaldehyde (Table 5, Entry 3)
2B.7 Mechanism of the Reaction:

2B.7.1 In case of phenyl acetic acid

The plausible mechanism for the said conversion involves formation of complex (1) with reaction of oxone and Iodobenzene in aqueous acetonitrile at room temperature. This complex (1) afterwards react with phenyl acetic acid with removal of Iodobenzene and CO₂ to formed benzyl alcohol which further oxidises to obtained benzaldehyde as product with good yield (Scheme 2B.8).

2B.7.2 In case of phenyl glycine

The plausible mechanism for the said conversion involves formation of complex (1) with reaction of oxone and Iodobenzene in aqueous acetonitrile at room temperature.

This complex (1) afterwards react with phenyl glycine with removal of Iodobenzene and CO₂ to formed imine intermediate which under goes hydrolysis to obtained benzaldehyde as product with good yield (Scheme 2B.9).
2B.7.3 In case of alpha alkyl or aryl phenyl acetic acid

The plausible mechanism for the invented conversion involves formation of complex (1) with reaction of oxone and Iodobenzene in aqueous acetonitrile at room temperature. This complex (1) afterwards react with α-methyl phenyl acetic acid with removal of Iodobenzene and CO₂ to formed secondary alcohol as intermediate which under goes further oxidation to obtained Acetophenone as product with good yield (Scheme 2B.10).

2B.8 Suggested Potential Applications of Methodology

This method could be useful in the synthesis of bioactive molecules, for example Amfebutamone (Bupropion), a species specific amfebutamone is synthesized with the route having ketone introduction step as shown in (Scheme 2B.11) in this synthesis bromine used for the α-bromination of ketone which react with ter-butylamine to formed amfebutamone. Bupropion lowers seizure threshold, and its potential to cause seizures has been widely publicized, Bupropion is an effective antidepressant.
1. Amfebutamone

![Scheme 2B.11](image)

2. Chlorphenoxamine

4-chloro benzophenone undergoes Grignard reaction to formed 1-(4-chlorophenyl)-1-phenylethanol which react with chloroethyldimamine and sodamine to obtain Chlorphenoxamine. Chlorphenoxamine is an antihistamine and anticholinergic used as an antipruritic and antiparkinsonian agent.

![Scheme 2B.12](image)

3. Ambrisentan

Drug indicated for use in the treatment of pulmonary hypertension. It functions as an endothelin receptor antagonist.
4) Amfetaminil

is a stimulant drug derived from amphetamine, which was developed in the 1970s and used for the treatment of obesity, ADHD and narcolepsy.

Monasterol

Monasterol is a cell-permeable small molecule inhibitor discovered by Thomas U. Mayer in the lab of Tim Mitchison. Monastrol was shown to inhibit the kinesin, a motor protein important for spindle bipolarity.
6) Anisindione.

Anisindione (brand name Miradon) is a synthetic anticoagulant and an indanedione derivative.
7) Amfenac

![Scheme 2B.17](image)

2B.9 Summary & Conclusion

A capable and novel method has been developed for oxidative decarboxylation of phenyl acetic acid and α- substituted phenyl acetic acid to benzaldehydes and ketones synthesize respectively using oxone and Iodobenzene in aqueous acetonitrile solvent system at room temperature. This is single reaction system in which all types of phenyl acetic acid, α-alkyl or aryl phenyl acetic acid and Mendalic acid as well as phenyl glycine under goes oxidative decarboxylation to achieve an excellent yield of desired products. Lower reaction time adds an additional credit to the present study. In general, all kinds of functional groups were very well tolerated giving higher Yields. The reaction was optimized with respect to various reaction parameters and enabled oxidative decarboxylation of various electron-rich, electron-deficient phenyl acetic acid and α-substituted phenyl acetic acid, affording excellent yields of the desired products, thus illustrating the broad applicability of the methodology. This method exhibits a broad scope, affords clean product in moderate to high yields and will be of great utility in organic synthesis.

The developed protocol might prove a hopeful alternative for oxidative decarboxylation for benzaldehydes and ketones synthesis.

In summary, we developed a new protocol for oxidative decarboxylation of phenyl acetic acid and α-alkyl or aryl phenyl acetic acid to obtained benzaldehydes and ketones as products by using hypervalent iodine (III) Species in situ with help of Oxone and Iodobenzene in an aqueous acetonitrile solvent system.
2B.10 Experimental Section:

2B.10.1 General experimental procedure for oxidative decarboxylation of phenyl acetic acid, α-hydroxy phenyl acetic acid and α-amino phenyl acetic acid to benzaldehyde:

Mixture of Oxone (614 mg, 2 mmol) and Iodobenzene (408 mg, 2 mmol) in aqueous acetonitrile stirred at room temperature for 10 min, followed by addition of substrate (1 mmol) under stirring at room temperature. The resultant reaction mixture was stirred at room temperature until the starting material was completely consumed (TLC). The reaction mixture was diluted with CH₂Cl₂ and washed successively with 10% sodium bicarbonate (2 x15 mL), followed by water (2 x20 mL). The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtained crude product. The pure product was obtained after silica gel column chromatography (10% EtOAc–Hexane).

2B.11 Characterization Data of aldehydes

IR and NMR data were identical with those of authentic sample and data are given below

**Benzaldehyde** (Table 5, Entry 1): Liquid, BP 177 °C .IR (KBr): 2791, 2732, 1702,1594,1431,1362 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ=10.00 (1H, s), 7.84 (2H, d, J = 7.0, ), 7.61 (1H, t, J = 7.3, ), 7.52(2H, t, J = 7.2, ).

**4-Methyl benzaldehyde** (Table 5, Entry 2): Liquid, 202 °C BP .IR (KBr): 2922, 2821, 2731, 1701, 1604, 1453,842,767,640 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ= 7.21(2H, d, J=7.8Hz), 7.66(2H, d, J=8.1Hz), 9.87(1H, s)
3, 5 dimethoxy benzaldehyde (Table 5, Entry 4):

Solid, IR (KBr): 2940, 2829, 2728, 1690, 1586, 1460, 866, 783 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ=7.43-7.37(2H, m), 6.95(1H, d, J=8.1Hz), 9.82(1H, s)

4-Chlorobenzaldehyde (Table 5, Entry 5): Solid, Mp 46 °C . IR (KBr): 2831, 2729, 1692, 1571, 1431, 1194, 896, 785, 676 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ=7.80(2H, d, J=8.1Hz), 7.50(2H, d, J=10Hz), 9.95(1H, s)

2-Naphthaldehyde (Table 5, Entry 5): Liquid, BP 152 °C . IR (KBr): 2951, 2931, 2859, 2722, 1689, 1573, 1461, 786 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ= 9.23(1H, d, J=8.7 Hz), 7.98-7.48(6H, m) 10.2(1H, s)

4-isopropylbenzaldehyde (Table 5, Entry 3): IR (KBr): 2962, 2877, 2730, 1700, 1604, 1460, 1215, 833 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ= 9.9 (s, 1H), 7.40-7.31 (m, 2H), 7.82-7.80 (m, 2H, ArH), 1.28 (6H, d, J=6.9); 3.0 (1H, q)
2B.10.2 typical procedure for decarboxylation of α-alkyl or aryl Phenyl acetic acid to ketones (Table 1, entry 8):

Mixture of Oxone (614 mg, 2 mmol) and Iodobenzene (204 mg, 1mmol) in aqueous acetonitrile stirred at room temperature for 10 min, followed by addition of α-alkyl or aryl phenyl acetic acid (1mmol) and catalytic amount of KBr (59 mg) under stirring at room temperature. Isolation and purification of the product was carried out by following above procedure.

2B.11.1 Characterization Data of Ketones

IR and NMR data were identical with those of authentic sample and data are given below.

Acetophenone (Table 5, Entry 8)

![Acetophenone structure]

Colorless liquid, (bp 202 °C), $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.94-7.92(d, $J = 7.8$Hz, 2H), 7.56-7.51(t, $J = 7.35$Hz, 1H), 7.45-7.40(t, $J = 7.5$Hz, 2H), 2.57(s, 3H) ppm. IR (KBr) $\nu_{\text{max}}$: 1683, 1490, 3066, 3031 and 1691 cm$^{-1}$.

Benzophenone (Table 5, Entry 10)

![Benzophenone structure]

Solid, MP 306 °C .IR (KBr): 2925, 2867, 2854,1668,1401,1365,940,700 cm$^{-1}$ $^1$H NMR (300 MHz, CDCl$_3$) $\delta$=7.8(2H, d, $J=6.9$Hz) 7.79-7.44(8H, m)
Propiophenone (Table 5, Entry 9):

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3})}: & \quad \delta 7.95-7.92 (d, \ J = 7.5 \text{ Hz}, 2H), \ 7.54-7.49 (t, \ J = 7.05 \text{ Hz}, 1H), \ 7.45-7.40 (t, \ J = 7.35 \text{ Hz}, 2H), \ 2.94-2.89 (t, \ J = 7.2 \text{ Hz}, 2H), \ 1.00-0.95 (t, \ J = 7.35 \text{ Hz}, 3H) \text{ ppm. IR (neat)} \ 1684, \ 1599, \ 1583, \ 1492, \ 761 \text{ and } 691 \text{ cm}^{-1} \\
\end{align*}
\]