Oxidation of olefins and hydrazones by anodically in situ generated manganese (III) acetate

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The oxidation of olefins and hydrazones of carbonyl compounds has been performed by using in situ anodically generated milder oxidant Mn(III) acetate at Pt electrode in acetic acid. The oxidation of acyclic olefins leads to the formation of 1,2-diacetate while in the case of cyclic olefin it results in the formation of γ-lactone ring onto double bond. Further, intermolecular carbolactonization of olefins has been achieved using more reactive carboxylic acid substrate i.e. ethyl hydrogen malonate at room temperature under the similar reaction conditions. Mn(III) acetate oxidation of hydrazones of carbonyl compounds leads to its fragmentation products.

Last three decades have witnessed a great deal of attention focussed on the oxidation of alkenes by metal ions. The reaction of manganese (III) acetate with alkenes in carboxylic acid solvents has been shown to be a valuable route to γ-lactone by several group of workers. The other companion metal ions e.g. cobalt (III), lead (IV) and cerium (IV) can respectively bring about this transformation only in lower yield. Inspite of high potentiality of Mn(III) acetate for oxidative carbon-carbon bond formation, practical usefulness of Mn(III) promoted oxidation in organic synthesis has been considerably limited because of instability of the manganese (III) salt, and troublesome treatment of the resulting large amount of Mn(OAc)$_2$.4H$_2$O due to its high molecular weight. In-cell electrochemical oxidative or reductive regeneration of metallic complexes turning into catalytic stoichiometric reaction is synthetically quite promising to tackle these problems. This was illustrated by two reported studies on the Mn (III)-promoted electrochemical addition of active methylene compounds to olefins in which Shundo et al. have demonstrated the carboxymethylation of styrene derivatives to γ-aryl-γ-lactones by Mn (III) mediated electrooxidation in a mixed solvent of glacial acetic acid and acetic anhydride. Later, Nedlec and also Steckhan with their coworkers utilized this milder methodology for the electrooxidative addition of various olefins for C-C-bond formation.

In view of the above it was of interest to carry out the oxidative reaction of anodically in situ generated manganese (III) acetate, a milder oxidant, with some olefins and hydrazones of carbonyl compounds. In the course of present investigation, Mn (III) mediated electrooxidation of olefins 1-3 and hydrazones 4-5 was carried out in acetic acid to afford products 1a-5a, 1b-3b in a good to excellent yield. The general reaction may be depicted as in Scheme I.

**Oxidation of olefins**

Mn (III) promoted electrooxidative addition of active methylene compounds to alkenes has been reported by Shundo et al.; the reaction was carried out in a beaker type of divided cell in a mixed solvent of glacial acetic acid and acetic anhydride.

In the present work, the electrolysis was carried...
out under different set of reaction conditions in a cell without diaphragm, a configuration of cell known to offer advantage over a cell with diaphragm. Anodic oxidation of cyclohexene, styrene and stilbene was achieved in glacial acetic acid containing manganese diacetate (0.01M) at 68-70°C using platinum foil as anode and cathode. The electrooxidation of cyclohexene results in the formation of γ-lactone 1a while

Table I—Reaction of electronically generated Mn(III) acetate and olefin 1-3 in acetic acid with and without ethyl hydrogen malonate and hydrazone 4-5 in acetic acid using platinum foil as anode and cathode (6.25 cm²), T = 25 or 70 ± 2°C.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Substrate (1-5)</th>
<th>Product (1a-5a, 1b-3b)</th>
<th>Current (mA)</th>
<th>Reaction period (hr)</th>
<th>Yield (%)</th>
<th>m.p./[b.p.] °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1a</td>
<td>40</td>
<td>13.4</td>
<td>50</td>
<td>[135°C/18mm]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lit.140 -45/20mm)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1b</td>
<td>40</td>
<td>13.4</td>
<td>65</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>CH=CH₂</td>
<td>2a</td>
<td>40</td>
<td>15</td>
<td>60</td>
<td>[156/18mm]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lit.159.5/18mm)</td>
</tr>
<tr>
<td>4</td>
<td>CH=CH₂</td>
<td>2b</td>
<td>40</td>
<td>15</td>
<td>66</td>
<td>a</td>
</tr>
<tr>
<td>5</td>
<td>C₆H₅</td>
<td>3a</td>
<td>40</td>
<td>6.12</td>
<td>49</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>C₆H₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lit.109–110)</td>
</tr>
<tr>
<td>6</td>
<td>C₆H₅</td>
<td>3b</td>
<td>40</td>
<td>6.12</td>
<td>65</td>
<td>a</td>
</tr>
<tr>
<td>7</td>
<td>Ph</td>
<td>4a</td>
<td>100</td>
<td>2.20</td>
<td>80</td>
<td>155-160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lit. 155-160)</td>
</tr>
<tr>
<td>8</td>
<td>CH₂</td>
<td>5a</td>
<td>30</td>
<td>11.03</td>
<td>74</td>
<td>235-237</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lit. 239-41)</td>
</tr>
</tbody>
</table>

a—Viscous liquid identified by spectral data.
styrene and stilbene were converted to their diacetate 2a, 3a brought about by the mediation of in situ generated Mn (III) acetate in the reaction medium. On the other hand, carboxethoxylactones 1b-3b of these olefins were obtained comparatively in better yield from Mn (III) mediated anodic coupling of olefins with ethyl hydrogen malonate using 0.75 equivalent mole of Mn(OAc)₂·4H₂O at room temperature (25°C) under similar experimental conditions. The ethyl hydrogen malonates serves as a reactive equivalent of acetic acid. The details of substrate, product and other experimental data are given in Table I.

The γ-lactones of the alkenes 1a, 1b, 2b and 3b in their IR spectra exhibit strong absorption band in the range of 1760-1780 cm⁻¹ assignable to C=O stretching of the lactone moiety while the diacetate of styrene 2a and stilbene 3a display absorption bands at 1741 cm⁻¹ and 1749 cm⁻¹ respectively which could be attributed to carbonyl of acetate group. These products 1a-3a and 1b-3b are also characterized by their NMR spectra given in Table II.

The anodic reaction of Mn(OAc)₂ can be depicted as,

\[
\text{Mn(OAc)}_2 + \text{AcOH} \rightarrow \text{Mn(OAc)}_3 + \text{H}^+ + \text{e}^- 
\]

The mechanism for the Mn(III) mediated coupling reactions appears to be complex and not yet fully understood. A plausible reaction pathway is suggested in Scheme II. The Mn(II) ion gets oxidized electrochemically to an active Mn(III) ion on the anode which give a carboxymethyl radical (II) species and a Mn(II) ion. According to earlier studies, this radical may get added to a carbon - carbon double bond of an olefin and generate a new radical intermediate which abstract hydrogen atom from the solvent to form a saturated coupling product (III).

In the presence of more reactive carboxylic substrate i.e., ethyl hydrogen malonate, a methine radical species (V) from ethyl hydrogen malonate (IV) may

<table>
<thead>
<tr>
<th>Compd</th>
<th>IR (Nujol) cm⁻¹</th>
<th>NMR (CDCl₃) 5, ppm</th>
<th>Found (Calc.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2940, 2850, 1780, 1180</td>
<td>4.2 (m, 1H, CHCO), 2.0-1.0 (m, 11H, C₆H₆CH₂)</td>
<td>68.43 7.91</td>
</tr>
<tr>
<td>1b</td>
<td>2940, 2845, 1773, 1185</td>
<td>4.67 (b, 1H, CHCOO), 4.20 (q, 2H, CH₂, CH₃), 3.30 (m, 1H, CHOCO), 2.63 (m, 1H, CHCHOOCO), 1.90 - 0.96 (m, 11H, 4xCH₂, CH₂CH₂CO₂)</td>
<td>62.18 7.46</td>
</tr>
<tr>
<td>2a</td>
<td>3466, 2961, 1741</td>
<td>2.05 (s, 3H, OCOCO₂), 2.2 (s, 3H, OCOCO₂), 5.0 (t, 1H, CH₂)</td>
<td>64.79 6.28</td>
</tr>
<tr>
<td>2b</td>
<td>3465, 2964, 1771</td>
<td>1.2 (t, 3H, CH₂CH₂CH₂), 2.05 (q, 2H, CH₂CH₂CO₂), 3.35 (s, 1H, CHCO₂Et), 4.15 (q, 2H, CO₂CH₂CH₂), 5.1 (t, 1H, CH₂CH₂), 7.45 (m, 5H Ar-H)</td>
<td>66.58 5.93</td>
</tr>
<tr>
<td>3a</td>
<td>3020, 1749</td>
<td>2.2 (s, 6H, OAc), 5.2 (s, 2H, 2xCH₂), 7.1-7.4 (m, 10H, Ar-H)</td>
<td>72.41 5.98</td>
</tr>
<tr>
<td>3b</td>
<td>3481, 1764, 1189</td>
<td>1.2 (t, 3H, CH₂CH₂), 2.05 (q, 2H, CH₂CH₂CO₂), 4.2 (q, 2H, CH₂CH₂CO₂), 4.95 (d, 1H, CH₂), 5.9 (d, 1H, OCH₂-Ar), 7.0-7.6 (m, 10H, Ar-H)</td>
<td>73.51 7.84</td>
</tr>
<tr>
<td>4a</td>
<td>1630, 1600, 1562</td>
<td>7.1 - 7.3 (m, 20H, Ar-H)</td>
<td>86.63 5.13</td>
</tr>
<tr>
<td>5a</td>
<td>2700, 1700</td>
<td>13.1 (bs, 1H, CO₂H), 7.4 - 8.0 (m, 4H, Ar-H)</td>
<td>53.81 3.18</td>
</tr>
</tbody>
</table>

Table II—IR, NMR and elemental data of products (1a-5a and 1b-3b)
be formed which can satisfactorily convert olefins to carboethoxylactones (Scheme III).

In addition to lactone formation substrates 2 and 3 tend to yield 1,2-diacetate. The earlier mechanistic study\(^9\) indicate that the diacetate products is a result of a single electron transfer oxidation as depicted in Scheme IV.

Fragmentation of hydrazones

Fragmentation of hydrazones 4, 5 took place smoothly by anodically in situ generated Mn (III) acetate in acetic acid medium containing hydrazones (0.1 M) and Mn (II) acetate (0.01 M) at \(-70^\circ C\) under the similar reaction conditions as described in the case of the oxidation of olefins. The reaction in this case may be visualized to be based on the capability of Mn (III) acetate to abstract acidic proton from the substrate finally to afford products 4a, 5a in good yield. The possible mechanistic route for the formation of benzophenone azine is given in Scheme V.

Under the similar reaction conditions hydrazone of p-chloroacetophenone 5 gave p-chlorobenzoic acid 5a. The IR spectra of hydrazone 4, 5 have been studied in the 4000-600 cm\(^{-1}\) region. In general, hydrazones exhibits a strong band for N-H stretching which is absent in the IR spectra of products 4a, 5a. The IR of p-chlorobenzoic acid shows strong absorption peak at 2700 and 1700 cm\(^{-1}\) characteristic of O-H and C=O stretching vibration. The NMR spectral data of azine 4a and p-chlorobenzoic acid 5a are given in Table II.

Experimental Section

Styrene (Aldrich), trans-stilbene (Aldrich), manganese(II) acetate (Merck) were used without further purification. Cyclohexene and hydrazones were prepared according to the established method. The compounds prepared were characterized by their physico-

chemical and spectroscopic properties. Melting points were determined in an open capillary tube in a Buchii apparatus and are uncorrected. IR spectra were recorded with Perkin-Elmer 783 grating spectrophotometer. The \(^1\)H NMR was run with JEOL FT-NMR spectrophotometer FX-90Q using TMS as internal standard (chemical shifts in \(\delta\), ppm).

General procedure for the reaction of anodically in situ generated Mn (III) acetate with olefins 1-3 and hydrazones 4, 5. Electrochemically generated Mn (III) acetate oxidizes olefins 1-3 and hydrazones 4, 5 in moderately good yield to their respective products. In a separate experiment the conversion of electrochemically in situ generated Mn (III) acetate from Mn (II) acetate in acetic acid was determined by iodometric titration. Figure 1 shows the plot of concentration of Mn (III) acetate in gm/lit vs electrolysis time. The concentration of Mn (III) acetate was found to increase with reaction time.

Electrolysis

The electrolysis was carried out under following

![Scheme III](image)

![Scheme V](image)
conditions: Cathode: Platinum foil (6.25 cm$^2$); Anode: Platinum foil (6.25 cm$^2$); Electrolyte: 0.1M sodium acetate in acetic acid (50 mL); Nature of cell: One compartment cell; Temperature: 70 or 25 ± 2°C.

Anodic oxidation of organic substrate (0.1M) was carried out in a solution containing sodium acetate used as electrolyte and Mn (II) acetate (0.01M) in acetic acid (50 mL) at 70 ± 2°C. The carboethoxylactonization of olefins 1, 2 and 3 was carried out in a solution containing olefins (1 equiv.), Mn (II) acetate (0.75 equiv.) and ethyl hydrogen malonate (3.5 equiv.) in acetic acid at 25°C. The solution was purged with nitrogen for 10 min and then it was set for electrolysis under constant current condition in a cell without diaphragm. The current (Table I) was passed using a DC regulated power supply for the calculated period of time with constant stirring. The electrolysis and other details of the reaction are given in Table I.

Work up and isolation of products

After the completion of reaction, the mixture was poured into cold water (50 mL) and was extracted thrice with ether (3x25 mL). The ether layer was washed with saturated solution of sodium bicarbonate repeatedly to remove acetic acid. It was dried on anhyd. Na$_2$SO$_4$, filtered and the solvent was stripped off on a rotavapour to yield products la-Sa, lb-3b. The products obtained were purified by column chromatography and identified on the basis of their physico-chemical and spectral data. The IR, NMR and elemental analysis are tabulated in Table II.

Acknowledgement

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References