Preparation of α-iodoacetates from alkenes by Co(OAc)$_2$ catalysed Woodward-Prevost reaction

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Woodward-Prevost reaction of alkenes with iodine and cobalt(II) acetate in acetic acid is reported. The reaction is facile and α-iodoacetates are obtained from both acyclic and cyclic alkenes in high yields within 15-55 min.

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Woodward-Prevost reaction is an important reaction in organic synthesis as an alkene reacts readily with silver acetate or silver benzoate and iodine in the presence of water to give a product corresponding to cis- or trans-hydroxylation via α-iodoacetate intermediates. α-Iodoacetates are equally important in organic synthesis as they can be transformed into other functional groups and in the C-C bond formation reactions. There are only a few methods available in the literature for their preparation. Metal acetates such as thallium(I) acetate, mercury(II) acetate, bismuth(III) acetate, copper(II) acetate, or other reagents such as mercury(II) oxide-acetic anhydride, peracetic acid-acetic acid/ethyl ether and CuO-HBF$_4$ in CH$_2$Cl$_2$/AcOH with I$_2$ and olefin, allow the isolation or detection of α-iodoacetates.

We now report a novel addition reaction of alkenes in the presence of iodine and cobalt(II) acetate to give the corresponding α-iodoacetates under normal conditions (Scheme I).

Earlier methods used the acetates of silver, thallium and mercury to get α-iodoacetates from olefins. Under normal conditions, these reactions generally require about 1 to 48 hr for completion depending on the nature of the metal acetate and the substrates used for the reaction.

Believing that the salts of cobalt may give the required product, we carried out the reaction of 1-hexene with iodine and cobalt(II) acetate in acetic acid by stirring at 25°C, and got the corresponding α-iodoacetates in high yields within 15 min. In order to extend this reaction to other alkenes, the reaction of 1, Co(OAc)$_2$, HOAc with different substituted alkenes was taken up and the results are presented in Table I.

From Table I, it is clear that, the reaction is general and different iodoacetates can be prepared under the above said reaction conditions from both acyclic and cyclic alkenes in high yields. It is also clear that, the reaction is selective in the sense that only the less substituted iodo product is obtained (entries 1, 3-7) from terminal olefins. Cyclic alkenes exclusively furnish the trans-iodoacetates (entries 8-10). All the compounds prepared by this procedure are characterized by IR and $^1$H NMR spectral analysis after purification.

A mild, convenient and selective method for the preparation of α-iodoacetates within short duration (15-55 min) has been developed by us using readily available, cobalt(II) acetate only by stirring at 25°C in excellent yields. We believe that this procedure is better and more practical alternative to the existing methodologies. Comparison of the results of the reaction of some representative alkenes by our procedure with that of the other reagents/metal acetates has been provided in Table II.

**Experimental Section**

All alkenes, cobalt(II) acetate and glacial acetic acid were obtained from Spectrochem and Rankem or prepared by standard procedures. IR spectra were recorded on Nicolet 4000 FT-IR spectrometer and $^1$H NMR spectra were recorded on 400 MHz, Bruker instrument and the chemical shift values (δ ppm) are reported relative to TMS in CDCl$_3$ as solvent.
Table 1 — α-Iodoacetoxylation of olefins with cobalt(II) acetate and iodine in acetic acid

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Time (min)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Hexene</td>
<td>20</td>
<td>1-iodo-2-acetoxyhexane</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>2,3-Dimethyl-2-butene</td>
<td>15</td>
<td>2-iodo-3-acetoxy-2,3-dimethylbutane</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>1-Heptene</td>
<td>25</td>
<td>1-iodo-2-acetoxyheptane</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>2-Octene</td>
<td>35</td>
<td>2-iodo-3-acetoxyoctane</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>1-Undecene</td>
<td>50</td>
<td>1-iodo-2-acetoxyundecane</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>PhCH=CH₂</td>
<td>55</td>
<td>PhCH(OAc)CH₂</td>
<td>78</td>
</tr>
<tr>
<td>7</td>
<td>PhCMe=CH₂</td>
<td>25</td>
<td>PhC(Me)(OAc)CH₂</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>Cyclohexene</td>
<td>15</td>
<td>trans-1-acetoxy-2-iodocyclohexane</td>
<td>88</td>
</tr>
<tr>
<td>9</td>
<td>Cyclooctene</td>
<td>20</td>
<td>trans-1-acetoxy-2-iodocyclooctane</td>
<td>79</td>
</tr>
<tr>
<td>10</td>
<td>Cyclooctadecene</td>
<td>25</td>
<td>trans-1-acetoxy-2-iodocyclooctadecene</td>
<td>92</td>
</tr>
</tbody>
</table>

*Isolated by column chromatography.

Table 2 — α-Iodoacetoxylation of some representative olefins with various reagents and iodine

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent(s)</th>
<th>Cyclohexene time/yield (%)</th>
<th>Styrene time/yield (%)</th>
<th>α-Methylstyrene time/yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cobalt(II) acetate</td>
<td>15 min/88</td>
<td>55 min/78</td>
<td>25 min/75</td>
</tr>
<tr>
<td>2</td>
<td>thallium(I) acetate</td>
<td>48 hr/78</td>
<td>48 hr/78</td>
<td>48 hr/78</td>
</tr>
<tr>
<td>3</td>
<td>bismuth(III) acetate</td>
<td>17.5 hr/84</td>
<td>-</td>
<td>17.5 hr/91</td>
</tr>
<tr>
<td>4</td>
<td>silver acetate</td>
<td>5-6 hr/70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>KOAc-AI₂O₃/CH₂Cl₂</td>
<td>42 hr/70</td>
<td>48 hr/75</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>NIS₂/AsOH/CH₂Cl₂</td>
<td>1 hr/75</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

§ Present method
* N-Iodosuccinimide

Preparation of 1-iodo-2-acetoxyhexane: General procedure

Cobalt(II) acetate (0.89 g, 5 mmole), glacial acetic acid (5 mL) and 1-hexene (0.84 g, 10 mmole) were taken in a 50 mL RB flask. Iodine (2.54 g, 10 mmole) in glacial acetic acid was added slowly to the above mixture and stirred at 25°C. The reaction was monitored by TLC (5 % EtOAc: pentane) and went to completion within 15 min. The product was extracted by ether (3 x 10 mL) and combined etheral extract was washed with 5 % aqueous sodium thiosulphate, saturated NaHCO₃ solution, water and dried over anhyd. sodium sulphate. After work-up, the crude product was subjected to silica gel chromatography and 1-iodo-2-acetoxyhexane was obtained in 2.59 g (96% yield). A similar procedure was followed for the other alkenes.

A summary of the yields (based on 10 mmole of starting alkene), IR and ¹H NMR spectral data of the products follows.

1-Iodo-2-acetoxyhexane: Obtained in 96% yield (2.59 g); IR (cm⁻¹): 1719, 1259, 1031, 415; ¹H NMR: 2.09 (s, -COCH₃), 3.20–3.39 (oct, -CH₂I), 4.83–4.89 (sex, -CHCOCH₃).

2-Iodo-3-acetoxy-2,3-dimethylbutane: Obtained in 90% yield (2.43 g); IR (cm⁻¹): 1719, 1279, 1166, 410; ¹H NMR: 1.29 [s, (CH₃)₂C(CH₂I)₃], 1.54 [s, (CH₃)₂Cl⁻], 2.20 (s, -COCH₃).

1-Iodo-2-acetoxyheptane: Obtained in 91% yield (2.58 g); IR (cm⁻¹): 1745, 1243, 1036, 498; ¹H NMR: 2.05 (s, -COCH₃), 3.99–4.06 (oct, -CH₂I⁻), 4.83–4.89 (sex, -CHCOCH₃).

2-Iodo-3-acetoxyoctane: Obtained in 90% yield (2.68 g); IR (cm⁻¹): 1755, 1238, 1031, 426; ¹H NMR: 2.07 (s, -COCH₃), 3.20–3.39 (m, -CH₂I⁻), 4.66–4.72 (quin, -CHCOCH₃).

1-Iodo-2-acetoxyundecane: Obtained in 89% yield (3.03 g); IR (cm⁻¹): 1745, 1243, 1000, 420; ¹H NMR: 2.18 (s, -COCH₃), 3.23–3.38 (oct, -CH₂I⁻), 4.66–4.74 (quin, -CHCOCH₃).

PhCH(OAc)CH₂I: Obtained in 78% yield (2.26 g); IR (cm⁻¹): 1755, 1233, 1062, 545; ¹H NMR: 2.08 (s, -COCH₃), 3.46–3.49 (m, -CH₂I⁻), 5.86–5.90 (m, -CHCOCH₃), 7.36–7.37 (m, 5H, Ph).
PhC(Me)(OAc)CH₂I: Obtained in 75% yield (2.28 g); IR (cm⁻¹): 1734, 1243, 1031, 545; ¹H NMR: 1.94 (s, -CH₃), 2.09 (s, -COCH₃), 3.25-3.28 (m, -CH₂I-), 7.26 (m, 5H, Ph).

trans-1-Acetoxy-2-iodocyclohexane: Obtained in 88% yield (2.36 g); IR (cm⁻¹): 1740, 1243, 1036, 420; ¹H NMR: 2.05 (s, -COCH₃), 3.99-4.06 (oct, -CHI-), 4.83-4.89 (s, -CHCOCH₃).

trans-1-Acetoxy-2-iodocyclooctane: Obtained in 79% yield (2.34 g); IR (cm⁻¹): 1734, 1243, 1047, 410; ¹H NMR: 2.07 (s, -COCH₃), 4.38-4.43 (hep, -CHI-), 5.19-5.23 (s, -CHCOCH₃).

trans-1-Acetoxy-2-iodocyclododecane: Obtained in 92% yield (3.24 g); IR (cm⁻¹): 1745, 1238, 721, 416; ¹H NMR: 2.09 (s, -COCH₃), 4.33-4.40 (hep, -CHI-), 4.83-4.87 (q, -CHCOCH₃).

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References