Short communication

Ruthenium(III) Chloride as an Efficient Catalyst for Conversion of Aldehydes to 1,1-diacetates Under Mild Conditions

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Abstract

Ruthenium(III) chloride catalyzes the preparation of 1,1-diacetates from aldehydes under mild and in solvent or solvent-free conditions. This method has some advantages such as good to excellent yields, ease of operation and workup, short reaction time, high catalytic efficiency and high chemoselectivity.

Keywords: 1,1-diacetates, acylals, protecting group, ruthenium(III) chloride, aldehyde, solvent-free condition

1. Introduction

Geminal diacetates (acylals) are stable under neutral and basic conditions\textsuperscript{1} and they are frequently used as protecting groups for aldehydes.\textsuperscript{2} 1,1-Diacetates are synthetically important precursors for the preparation of 1-acetoxy dienes for Diels–Alder reaction.\textsuperscript{3} The acyloxy groups in acylals can be converted into other useful functional groups by reaction with appropriate nucleophiles.\textsuperscript{4,5} Recently, palladium-catalyzed asymmetric allylic alkylation of acylals was applied for the total synthesis of saphingofungins E and F.\textsuperscript{6} In addition, indium-mediated alkylation of gem-diacetates and palladium-catalyzed substitution reactions of geminal allylic diacetates have also been reported.\textsuperscript{7}

Several reagents or catalysts such as InBr\textsubscript{3},\textsuperscript{8} Cu(OTf)\textsubscript{2},\textsuperscript{9} NBS,\textsuperscript{10} Bi(NO\textsubscript{3})\textsubscript{3} \cdot 5H\textsubscript{2}O,\textsuperscript{11} In(OTf)\textsubscript{3},\textsuperscript{12} Bi(OTf)\textsubscript{3} \cdot x H\textsubscript{2}O,\textsuperscript{13} zirconium sulfophenyl phosphonate,\textsuperscript{14} H\textsubscript{2}NSO\textsubscript{3}H,\textsuperscript{15} LiBF\textsubscript{4},\textsuperscript{16} zirconium sulfophenyl phosphonate,\textsuperscript{17} Zn(OTf)\textsubscript{2} \cdot 6H\textsubscript{2}O,\textsuperscript{18} sulfated zirconia\textsuperscript{19} and heteropolycompounds such as Wells–Dawson acid,\textsuperscript{20} P\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{21} HClO\textsubscript{4} \cdot SiO\textsubscript{2},\textsuperscript{22} erbium triflate\textsuperscript{23} and 12-molybdophosphoric acid\textsuperscript{24} have been employed for the synthesis of acylals from aldehydes using acetic anhydride.

Ruthenium(III) chloride has been used as a catalyst for oxidation of tertiary amines,\textsuperscript{25} alcohols\textsuperscript{26–28} and phosphorus acid.\textsuperscript{29} Recently, this catalyst was applied for the synthesis of 2-ethyl-3-methylquinolines from anilines and trialkylamine\textsuperscript{30} and for acylation of alcohols, phenols, thiols and amines.\textsuperscript{31}

In this work, we wish to report a mild, facile and efficient method for conversion of aldehydes to corresponding acylals using acetic anhydride in the presence of catalytic amounts of ruthenium(III) chloride hydrate without solvent or in n-hexane at room temperature.

2. Experimental

General: Starting materials and ruthenium(III) chloride were purchased from Fluka, Merck and Aldrich. The diacetate products were characterized by their spectral (IR, \textsuperscript{1}H–NMR), TLC and physical data. IR spectra (KBr pellets) were recorded on Bruker Equinox 55 FTIR spectrometer. NMR spectra were obtained on a Bruker Avance 400 MHz or Hitachi-Perkin Elmer, R-24B, 60 MHz.

Typical procedure for preparation of 1,1-diacetoxy-1-(2,6-dichlorophenyl)methane from 2,6-dichloro-
benzaldehyde: In a mortar, a mixture of 2,6-dichlorobenzaldehyde (0.525 g, 3 mmol), acetic anhydride (0.6 mL, 6 mmol), and RuCl₃ · xH₂O (0.018 g) was pulverized for 5 minutes. The reaction progress was followed by TLC (eluent: chloroform). After 5 minutes of pulverization, the conversion was above 99%. After completion of the reaction, silica gel (1.5 g) and chloroform (24 mL) were added to the mixture and filtered. The solvent was evaporated to give the pure product as a white solid. The solid was re-crystallized from a mixture of ethanol and water. Yield: 0.71 g (87%), m.p: 88–89 °C. [Lit²¹ m.p: 88–89 °C].

3. Results and Discussion

At the beginning, in order to evaluate various Lewis acids as potential catalysts in the acylal formation, we have investigated their efficiency in a model reaction between acetic anhydride (6 mmol) and 3-nitrobenzaldehyde (3 mmol) at room temperature under grinding conditions. Among the screened catalysts, RuCl₃ · xH₂O was found to be superior (Table 1, entry 14). It seems that not only the Lewis acidity of RuCl₃ · xH₂O is stronger than that of other catalysts used, but also for the conversion the necessary amount of RuCl₃ · xH₂O can be lesser than that of other catalysts. On the other hand, unfortunately, this very active catalyst is not reusable due to its high absorbency potential.

For a demonstration of the generality and ability of this catalyst, a variety of aliphatic and aromatic aldehydes were converted into acylals using catalytic amount of ruthenium(III) chloride hydrate (Scheme 1, Table 2). All products were known and characterized by their spectral data (IR, ¹H–NMR and MS) and by comparison to the authentic samples. The results reveal that ruthenium(III) chloride catalyzed reactions generally result in good yields with aromatic aldehydes incorporating electron-withdrawing substituents. It is important to mention that other methods such as AlPW₁₂O₄₀-catalyzed reactions³⁵ have provided poor yields in the presence of electron-withdrawing substituents.

Cyclohexanone, 4-nitroacetophenone and 4-acetylbenzaldehyde were also checked for the reactivity. The keto groups of these compounds have not reacted neither under room temperature nor reflux conditions. We suggest that the chemoselective protection of aldehydes in the presence of ketones can be achieved by this method (Scheme 2).

However, 4-(N,N-dimethylamino)benzaldehyde failed to give the expected acylal under grinding condition at room temperature or under reflux. The explanation for this result may be due to the strong electron donating properties of the dimethylamino group which will reduce the reactivity. It should be stressed that phenolic group was also protected as acetate in hydroxyl containing aromatic aldehyde (Table 2, entries 8 and 15) under such conditions.

Table 1: Conversion of 3–nitrobenzaldehyde to corresponding acylal by various catalysts.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>condition/solvent</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75% P₂O₅/SiO₂ (0.45 g)³²</td>
<td>r.t., grinding</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>Zr(HSO₄)₄ (4 mol %)³³</td>
<td>r.t., grinding</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>Al(HSO₄)₃ (5 mol %)³⁴</td>
<td>r.t., grinding</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>FeCl₃ (40 mol %)</td>
<td>r.t., grinding</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>AlCl₃ (40 mol %)</td>
<td>r.t., grinding</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>ZnCl₂ (40 mol %)</td>
<td>r.t., grinding</td>
<td>64</td>
</tr>
<tr>
<td>7</td>
<td>SnCl₄ (40 mol %)</td>
<td>r.t., grinding</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>SbCl₅ (40 mol %)</td>
<td>r.t., grinding</td>
<td>75</td>
</tr>
<tr>
<td>9</td>
<td>BF₃ · Et₂O (40 mol %)</td>
<td>r.t., grinding</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>RuCl₃ · H₂O (0.03 g)</td>
<td>r.t., grinding</td>
<td>89</td>
</tr>
<tr>
<td>11</td>
<td>RuCl₃ · H₂O (0.025 g)</td>
<td>r.t., grinding</td>
<td>90</td>
</tr>
<tr>
<td>12</td>
<td>RuCl₃ · H₂O (0.022 g)</td>
<td>r.t., grinding</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td>RuCl₃ · H₂O (0.02 g)</td>
<td>r.t., grinding</td>
<td>88</td>
</tr>
<tr>
<td>14</td>
<td>RuCl₃ · H₂O (0.018 g)</td>
<td>r.t., grinding</td>
<td>88</td>
</tr>
<tr>
<td>15</td>
<td>RuCl₃ · H₂O (0.015 g)</td>
<td>r.t., grinding</td>
<td>80</td>
</tr>
<tr>
<td>16</td>
<td>RuCl₃ · H₂O (0.013 g)</td>
<td>r.t., grinding</td>
<td>78</td>
</tr>
<tr>
<td>17</td>
<td>RuCl₃ · H₂O (0.01 g)</td>
<td>r.t., grinding</td>
<td>70</td>
</tr>
<tr>
<td>18</td>
<td>RuCl₃ · H₂O (0.018 g)</td>
<td>reflux/n–hexane</td>
<td>67</td>
</tr>
<tr>
<td>19</td>
<td>RuCl₃ · H₂O (0.018 g)</td>
<td>reflux/CH₃Cl</td>
<td>56</td>
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<tr>
<td>20</td>
<td>RuCl₃ · H₂O (0.018 g)</td>
<td>reflux/CH₂CN</td>
<td>62</td>
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</table>
Sheikhan et al.: Ruthenium(III) Chloride as an Efficient Catalyst for Conversion of Aldehydes ...
In our proposed mechanism, RuCl₃·xH₂O activates the carbonyl group of aldehydes very fast (Scheme 3). On the other hand, wet or supported RuCl₃, cannot catalyze acyl formation reaction.

4. Conclusion

We have established a mild and facile catalytic method for the synthesis of diacetates from aldehydes using ruthenium(III) chloride as an efficient heterogeneous inorganic catalyst at room temperature. Advantages of this method include high catalytic efficiency, the observed chemoselectivity, good to excellent yields, short reaction times and ease of operation and work-up.

5. Acknowledgement

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6. References