A facile one-pot four-component synthesis of dihydropyrrol-2-ones using \( \text{Cl}_3\text{CCO}_2\text{H} \)

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**ABSTRACT**

A convenient synthesis of different types of polyfunctional dihydropyrrol-2-ones via one-pot four component reactions of formaldehyde, dialkyl acetylenedicarboxylates and amines, catalyzed by trichloroacetic acid (\( \text{Cl}_3\text{CCO}_2\text{H} \)) at room temperature has been investigated. The significant advantages of this synthetic method are mild reaction conditions, available and inexpensive material, short reaction times, good yields, simple work-up.

**Keywords:** Dihydro-2-oxypyrroles, Dialkyl acetylenedicarboxylate, Amine, Aldehyde.

1. **Introduction**

Heterocyclic rings containing nitrogen atoms are abundant in nature and of great importance to life because their structural subunit exists in many bioactive nuclei [1]. Amongst the heterocycles containing nitrogen, dihydro-2-oxypyrroles are attractive compounds that have been used as antitumor and anticancer agents [2], HIV integrase [3], pesticides [4], antibiotics [5], herbicidal [6]. Due to their abundance in biologically important substances [7-9], they are in some of natural products and have extensive applications in medicinal, agriculture, and organic chemistry [10-14] (Scheme 1).

Jiang et al have reported synthesis of multisubstituted polyfunctional dihydropyrrol-2-ones via a one-pot four-component reaction in good to excellent yields from acetylenic esters, amines and aldehydes, for the first time [15]. This reaction has been developed by employing molecular iodine (I\(_2\)) [16], titanium dioxide (\( \text{TiO}_2 \)) nanopowder [17], \( \text{Cu(OAc)}_2\cdot\text{H}_2\text{O} \) [18], HOAc[19], TsOH [20], urea/HOAc [21]. Nevertheless, these methods are limited and organic solvents are used. Therefore, there is still the requirement to develop green, mild and efficient protocols for the synthesis of dihydro-2-oxypyrroles.

Herein, we present efficient methods for the one-pot, multicomponent synthesis of dihydro-2-oxypyrroles in the presence of trichloroacetic acid (\( \text{Cl}_3\text{CCO}_2\text{H} \)) as a catalyst under mild conditions.

2. **Experimental**

2.1. **Instruments**

Melting points and IR spectra were measured on an Electrothermal 9100 apparatus and a JASCO FT/IR-460 plus spectrometer, respectively. The \(^1\text{HNMNR}\) spectra were recorded on a Bruker DRX-400 Avance instrument with CDCl\(_3\) as solvent and using TMS as internal reference at 400 MHz. All reagents and solvents obtained from Fluka and Merck were used without further purification.

2.2. **General procedure for the synthesis of dihydro-2-oxypyrroles 4a-l**

A mixture of amine 1 (1.0 mmol) and dialkyl acetylenedicarboxylate 2 (1.0 mmol) in methanol (3 mL) was stirred for 20 min. Next, amine 1 (1.0 mmol), formaldehyde 3 (37% solution, 1.5 mmol), and \( \text{Cl}_3\text{CCO}_2\text{H} \) (10 mol %) were added respectively. The reaction mixture was allowed to stir at ambient temperature for the appropriate time (see Table 5). The progress of the reaction was monitored by thin-layer chromatography (TLC).
After completion of the reaction, the thick precipitate was filtered off and washed with ethanol (3 × 2 mL) to give the pure product 4.

2.3. General procedure for the synthesis of dihydro-2-oxopyrroles 7a–h

A mixture of amine 5 (1.0 mmol) and dialkyl acetylenedicarboxylate 2 (1.0 mmol) in methanol (3 mL) was stirred for 20 min. Next, amine 6 (1 mmol), formaldehyde 3 (1.5 mmol) and Cl\(_2\)CCO\(_2\)H (10 mol %) were added successively. The reaction mixture was stirred at ambient temperature for the appropriate time. The progress of the reaction was monitored by TLC. After completion, the solid precipitate was separated and washed with ethanol (3 × 2 mL) to give the pure product 7.

Selected spectral data

**Methyl 2,5-dihydro-5-oxo-1-phenyl-4-(phenylamino)-1H-pyrrole-3-carboxylate (4a):**

White powder. \(\text{\textsuperscript{1}H}NMR (400 MHz, CDCl\(_3\)): \delta = 3.76 (3H, s, OCH\(_3\)), 4.57 (2H, s, CH\(_2\)), 7.16–7.23 (4H, m, ArH), 7.34 (2H, t, \(J = 8.0\) Hz, ArH), 7.42 (2H, t, \(J = 8.0\) Hz, ArH), 7.81 (2H, d, \(J = 8.0\) Hz, ArH), 8.05 (1H, br s, NH) ppm.

**Methyl 4-(4-bromophenylamino)-1-(4-bromophenyl)-2,5-dihydro-5-oxo-1H-pyrrole-3-carboxylate (4d):**

Yellow solid. \(\text{\textsuperscript{1}H}NMR (400 MHz, CDCl\(_3\)): \delta = 3.78 (3H, s, OCH\(_3\)), 4.50 (2H, s, CH\(_2\)), 7.08 (2H, d, \(J = 8.8\) Hz, ArH), 7.30 (2H, d, \(J = 8.4\) Hz, ArH), 7.35 (2H, d, \(J = 8.8\) Hz, ArH), 7.72 (2H, d, \(J = 8.8\) Hz, ArH), 8.03 (1H, br s, NH) ppm.

**Ethyl 4-(p-tolylamino)-2,5-dihydro-5-oxo-1-p-tolyI-1H-pyrrole-3-carboxylate (4e):**

Yellow powder. \(\text{\textsuperscript{1}H}NMR (400 MHz, CDCl\(_3\)): \delta = 1.25 (3H, t, \(J = 7.2\) Hz, OCH\(_2\)CH\(_3\)), 2.36 (3H, s, CH\(_3\)), 2.37 (3H, s, CH\(_3\)), 4.23 (2H, t, \(J = 7.2\) Hz, OCH\(_2\)CH\(_3\)), 4.52 (2H, s, CH\(_2\)), 7.06 (2H, d, \(J = 8.4\) Hz, ArH), 7.14 (2H, d, \(J = 8.0\) Hz, ArH), 7.21 (2H, d, \(J = 8.4\) Hz, ArH), 7.69 (2H, d, \(J = 8.8\) Hz, ArH), 8.01 (1H, br s, NH) ppm.

**Methyl 4-(benzylamino)-2,5-dihydro-5-oxo-1-phenyl-1H-pyrrole-3-carboxylate (7a):**

White powder. \(\text{\textsuperscript{1}H}NMR (400 MHz, CDCl\(_3\)): \delta = 3.80 (3H, s, OCH\(_3\)), 4.48 (2H, s, CH\(_2\)-N), 5.10 (2H, d, \(J = 6.4\) Hz, CH\(_2\)-NH), 6.95 (1H, br, NH), 7.18–7.41 (8H, m, ArH), 7.73 (2H, d, \(J = 8.0\) Hz, ArH) ppm.

**Methyl 1-(4-bromophenyl)-4-(butylamino)-2,5-dihydro-5-oxo-1H-pyrrole-3-carboxylate (7f):**

Yellow powder. \(\text{\textsuperscript{1}H}NMR (400 MHz, CDCl\(_3\)): \delta = 0.96 (3H, t, \(J = 7.2\) Hz, CH\(_3\)), 1.41 (2H, sextet, \(J = 7.2\) Hz, CH\(_2\)), 1.61 (2H, quintet, \(J = 7.2\) Hz, CH\(_2\)), 3.80 (3H, s, OCH\(_3\)), 3.86 (2H, t, \(J = 7.2\) Hz, CH\(_2\)-NH), 4.41 (2H, s, CH\(_2\)-N), 6.77 (1H, br, NH), 7.50 (2H, d, \(J = 8.4\) Hz, ArH), 7.73 (2H, d, \(J = 8.4\) Hz, ArH) ppm.

3. Results and Discussion

In continuation of our ongoing researches [22–30], we utilized Cl\(_2\)CCO\(_2\)H as an efficient catalyst, for the one-pot four component synthesis of dihydro-2-oxopyrroles from condensation between formaldehyde, dialkyl acetylenedicarboxylates and amines at room temperature under mild conditions.

At first, we carried out the reaction of formaldehyde, aniline, and dimethyl acetylenedicarboxylate as a model reaction to optimize the reaction conditions in methanol at room temperature. The effects of various catalysts such as ZrCl\(_4\), ZrO\(_2\).2H\(_2\)O, Bi(\(\text{NO}_3\))\(_2\).5H\(_2\)O, ZnO, Al\(_2\)O\(_3\)-Cl, NaF, Cl\(_2\)CCO\(_2\)H, H\(_2\)BO\(_3\), TiO\(_2\), Zn(OAc)\(_2\).2H\(_2\)O and Zr(\(\text{NO}_3\))\(_2\) were studied. Of these, Cl\(_2\)CCO\(_2\)H found to be the most effective for this transformation (Table 1). Different amounts of Cl\(_2\)CCO\(_2\)H were used to achieve the best result was obtained by carrying out the reaction using 10 mol % of Cl\(_2\)CCO\(_2\)H (Table 2).

Based on these optimized reaction conditions, the generality of this reaction was investigated using several types of anilines (with various substituents) with dimethyl/diethyl acetylenedicarboxylate and formaldehyde under same conditions and the corresponding dihydro-2-oxopyrrole derivatives (5a–l) were synthesized in good yields (Scheme 2, Table 3). Also, we developed this synthetic method using two different amines (anilines and aliphatic amines) for the synthesis of dihydro-2-oxopyrrole (Scheme 3). The results are summarized in Table 4. Anilines bearing either electron-withdrawing functional groups (such as Cl, Br, F), or electron-donating ones (such as methyl, methoxy), and aliphatic amines, such as benzylamine, cyclohexylamine and \(n\)-butylamine were converted into the corresponding products with good to high yields.
Table 1. Optimization of catalyst on model reaction.\textsuperscript{a}

\begin{center}
\begin{tabular}{cccc}
Entry & Catalyst & Solvent & Temperature (°C) & Yield (\%)\textsuperscript{b} \\
\hline
1 & ZrCl\textsubscript{4} & MeOH & r.t & 70 \\
2 & ZrOCl\textsubscript{2}.8H\textsubscript{2}O & MeOH & r.t & 20 \\
3 & Bi(NO\textsubscript{3})\textsubscript{3}.5H\textsubscript{2}O & MeOH & r.t & 22 \\
4 & ZnO & MeOH & r.t & 35 \\
5 & Al\textsubscript{2}O\textsubscript{3}-Cl & MeOH & r.t & 30 \\
6 & NaF & MeOH & r.t & 31 \\
7 & Cl\textsubscript{3}CCO\textsubscript{2}H & MeOH & r.t & 91 \\
8 & H\textsubscript{3}BO\textsubscript{3} & MeOH & r.t & 34 \\
9 & TiO\textsubscript{2} & MeOH & r.t & 28 \\
10 & Zn(OAc)\textsubscript{2}.2H\textsubscript{2}O & MeOH & r.t & 48 \\
11 & Zr(NO\textsubscript{3})\textsubscript{2} & MeOH & r.t & 10 \\
\end{tabular}
\end{center}

\textsuperscript{a}Reaction conditions: aniline (2.0 mmol), DMAD (1.0 mmol), formaldehyde (1.5 mmol) with 10 mol\% catalyst for 24 h at room temperature.

\textsuperscript{b}Isolated yields.

Table 2. Optimization of reaction conditions.\textsuperscript{a}

\begin{center}
\begin{tabular}{cccc}
Entry & Catalyst (mol \%) & Solvent & Time (h) & Yield (\%)\textsuperscript{b} \\
\hline
1 & 5 & MeOH & 4 & 84 \\
2 & 10 & MeOH & 4 & 91 \\
3 & 10 & - & 6 & 42 \\
4 & 15 & MeOH & 4 & 88 \\
5 & 20 & MeOH & 4.5 & 85 \\
6 & 20 & EtOH & 5 & 75 \\
7 & 20 & EtOAc & 6 & 51 \\
8 & 20 & H\textsubscript{2}O/EtOH & 5 & 54 \\
9 & 20 & H\textsubscript{2}O & 6 & 20 \\
10 & 25 & MeOH & 4.5 & 81 \\
11 & 30 & MeOH & 5 & 79 \\
\end{tabular}
\end{center}

\textsuperscript{a}Reaction conditions: aniline (2.0 mmol), DMAD (1.0 mmol), formaldehyde (1.5 mmol) with Cl\textsubscript{3}CCO\textsubscript{2}H as catalyst at room temperature.

\textsuperscript{b}Isolated yields.
Scheme 2. Synthesis of highly functionalized dihydro-2-oxypyrroles 4a-l using anilines.

Table 3. Synthesis of highly functionalized dihydro-2-oxypyrroles 4a-l using anilines.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>R¹</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Lit. m.p.</th>
<th>[Ref.]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Me-C₆H₄</td>
<td>Me</td>
<td>4a</td>
<td>3</td>
<td>65</td>
<td>173-176</td>
<td>177-178</td>
<td>[16]</td>
</tr>
<tr>
<td>2</td>
<td>4-MeO-C₆H₄</td>
<td>Me</td>
<td>4b</td>
<td>5</td>
<td>64</td>
<td>179-181</td>
<td>176-177</td>
<td>[23]</td>
</tr>
<tr>
<td>3</td>
<td>4-Cl-C₆H₄</td>
<td>Me</td>
<td>4c</td>
<td>4</td>
<td>84</td>
<td>173-176</td>
<td>173-174</td>
<td>[16]</td>
</tr>
<tr>
<td>4</td>
<td>4-Br-C₆H₄</td>
<td>Me</td>
<td>4d</td>
<td>4</td>
<td>94</td>
<td>161-164</td>
<td>179-180</td>
<td>[15]</td>
</tr>
<tr>
<td>5</td>
<td>4-Me-C₆H₄</td>
<td>Et</td>
<td>4e</td>
<td>3.5</td>
<td>60</td>
<td>135-138</td>
<td>131-132</td>
<td>[15]</td>
</tr>
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<td>6</td>
<td>4-F-C₆H₄</td>
<td>Et</td>
<td>4f</td>
<td>3.5</td>
<td>87</td>
<td>170-172</td>
<td>172-173</td>
<td>[15]</td>
</tr>
<tr>
<td>7</td>
<td>4-Br-C₆H₄</td>
<td>Et</td>
<td>4g</td>
<td>3</td>
<td>76</td>
<td>170-172</td>
<td>169-171</td>
<td>[15]</td>
</tr>
<tr>
<td>8</td>
<td>4-MeO-C₆H₄</td>
<td>Et</td>
<td>4h</td>
<td>5</td>
<td>73</td>
<td>151-154</td>
<td>152-154</td>
<td>[23]</td>
</tr>
<tr>
<td>9</td>
<td>Ph</td>
<td>Et</td>
<td>4i</td>
<td>4</td>
<td>95</td>
<td>128-130</td>
<td>138-140</td>
<td>[15]</td>
</tr>
<tr>
<td>10</td>
<td>4-F-C₆H₄</td>
<td>Me</td>
<td>4j</td>
<td>3</td>
<td>87</td>
<td>162-1665</td>
<td>163-165</td>
<td>[28]</td>
</tr>
<tr>
<td>11</td>
<td>4-Cl-C₆H₄</td>
<td>Et</td>
<td>4k</td>
<td>3</td>
<td>62</td>
<td>169-172</td>
<td>168-170</td>
<td>[24]</td>
</tr>
<tr>
<td>12</td>
<td>Ph</td>
<td>Me</td>
<td>4l</td>
<td>4</td>
<td>91</td>
<td>153-156</td>
<td>155-156</td>
<td>[16]</td>
</tr>
</tbody>
</table>

*aYields refer to the pure isolated products.

*bAll known products reported previously in the literature were characterized by comparison of m.p., IR and $^1$HNMR spectra with those of authentic samples.

Scheme 3. Synthesis of highly functionalized dihydro-2-oxypyrroles 7a-h using two different amines.

The suggested mechanism for this transformation is depicted in Scheme 4. The reaction between amine and dialkyl acetylenedicarboxylate gives enamine A (Michael addition), and also reaction of amine with formaldehyde give imine B. Enamine A attacks to imine and generates C, which converts to intermediate D. Finally, intermediate D tautomerizes and produces the corresponding dihydropyrrole 5.

To compare the efficiency and applicability of Cl₃CCOOH with the reported catalysts and conditions in the literature for the synthesis of highly functionalized dihydro-2-oxypyrroles, we have tabulated the results of these catalysts in Table 5. As shown in Table 3, Cl₃CCOOH can act as efficient catalyst with respect to reaction times and yields of products.

4. Conclusions

In conclusion, trichloroacetic acid (Cl₃CCOOH) was found to be an efficient catalyst for the one-pot four-component reaction of formaldehyde, dialkyl acetylene dicarboxylates and amines to afford polyfunctionalized dihydropyrrrol-2-ones in good yields. The main advantages of the present synthetic method are mild reaction conditions, available and inexpensive material, short reaction times, good yields and easy reaction work-up procedure.
Table 4. Synthesis of highly functionalized dihydro-2-oxypyrroles 7a-h using two different amines.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R²</th>
<th>R¹</th>
<th>Ar¹</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Lit. m.p. (°C)</th>
<th>[Ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCH₂</td>
<td>Me</td>
<td>Ph</td>
<td>7a</td>
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<td>74</td>
<td>138-140</td>
<td>140-141</td>
<td>[15]</td>
</tr>
<tr>
<td>2</td>
<td>PhCH₂</td>
<td>Me</td>
<td>4-Br-C₆H₄</td>
<td>7b</td>
<td>4</td>
<td>88</td>
<td>126-128</td>
<td>120-121</td>
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</tr>
<tr>
<td>3</td>
<td>PhCH₂</td>
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<td>Cyclohexyl</td>
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<td>7d</td>
<td>4.5</td>
<td>92</td>
<td>121-124</td>
<td>123-124</td>
<td>[16]</td>
</tr>
<tr>
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<td>n-C₄H₉</td>
<td>Me</td>
<td>Ph</td>
<td>7e</td>
<td>3</td>
<td>86</td>
<td>68-70</td>
<td>60</td>
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</tr>
<tr>
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<td>7g</td>
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<td>82</td>
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<td>8</td>
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<td>4-F-C₆H₄</td>
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</tbody>
</table>

*a*Yields refer to the pure isolated products.  
*b*All known products reported previously in the literature were characterized by comparison of m.p., IR and ¹H NMR spectra with those of authentic samples.

![Scheme 4](image-url)

Scheme 4. Suggested mechanism for the synthesis of dihydro-2-oxypyrroles 7.

Acknowledgements

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References

Table 5. Comparison result of Cl$_3$CCO$_2$H with the reported catalysts in literature for the synthesis of highly functionalized dihydro-2-oxypyrroles 4i and 4l.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<td>4i</td>
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<td>95</td>
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</tr>
<tr>
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<td>EtOH/ 70 ºC</td>
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<td>85</td>
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<td>[22]</td>
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<td>[15]</td>
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<td>[22]</td>
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<td></td>
<td>Al(H$_2$PO$_4$)$_3$</td>
<td>MeOH, r.t.</td>
<td>5</td>
<td>81</td>
<td>[23]</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>InCl$_3$</td>
<td>MeOH, r.t.</td>
<td>3</td>
<td>85</td>
<td>[27]</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>[n-Bu$_4$N][HSO$_4$]</td>
<td>MeOH, r.t.</td>
<td>4</td>
<td>88</td>
<td>[24]</td>
</tr>
</tbody>
</table>