A SIMPLE AND COST EFFECTIVE SYNTHESIS OF
2-CYCLOPENTADIENYLIDEN-1,3-DIOXOLANE

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Abstract: A highly efficient preparation of 2-cyclopentadienyliden-1,3-dioxolane
from cyclopentadiene and 2-chloroethyl chloroformate has been achieved.
Reaction of two equivalents of sodium cyclopentadienide and KOH with 2-
chloroethyl chloroformate at 0.1 M produce the highest yield of this fulvene.

6-Heterosubstituted fulvenes are of intrinsic interest as sources of a variety of 7-
substituted bicyclo[2.2.1]heptanes and have functioned as useful synthetic
intermediates.1 A conventional application utilizes 6-acetoxyfulvene to synthesize
Corey's aldehyde.2 Alternatively, 2-cyclopentadienyliden-1,3-dithiolane 1, i.e. a
6,6-diheterosubstitued fulvene, has also been exploited as an active diene in the
Diels-Alder reactions.3

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Our recent works have demonstrated the intriguing and different chemoselectivities of 2-cyclopentadienyliden-1,3-dioxolane 2 in [6+3] and [6+4] cycloaddition reactions. In contrast to the Diels-Alder reaction of fulvenes and pyrones, the fulveneketene acetal 2 reacts with α-pyrene to yield the [6+4] cycloaddition adduct and this constitutes an efficient and novel route to azulenols.\(^4\) Alternatively, the transition metal mediated cycloaddition of 2-oxyallyl cations to electron rich fulveneketene acetal 2 provides an efficient route to the indan ring system.\(^5\) The fulvene 2 has been prepared by two different pathways owing to the interest in its physical properties (Scheme 1 and 2).\(^6,7\) However, these two low-yield syntheses either start from nickelocene and CF\(_3\)I (i.e. two compounds that either must be purchased at a costly price or prepared)\(^8\) or are associated with tedious procedures which have limited research on this intriguing compound.\(^9\) Therefore, a feasible method must be developed to prepare the fulvene 2. We report herein a new approach to 2 which avoids the above problems. The reaction is practical and can be performed on hundred-gram scale.

**Scheme 1**

\[
\begin{align*}
\text{KOH/DME} & \quad \text{NiCl}_2 \cdot 6\text{H}_2\text{O}, \text{DMSO} \\
\text{K}^+ & \quad 1) \text{H}^+; 30-50\%
\end{align*}
\]

\[
\begin{align*}
\text{Ni} & \quad + \text{CF}_3\text{I} + 2 \text{PPh}_3 \\
& \quad 55\%
\end{align*}
\]

\[
\begin{align*}
& \quad \text{(+)} \\
& \quad \text{Ph}_3\text{P} \quad \text{PPh}_3
\end{align*}
\]

\[
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{OH} & \quad 77\%
\end{align*}
\]

\[
\begin{align*}
\text{2}
\end{align*}
\]
In 1988, Neidlein reported on a facile synthesis of ketene acetalts by reacting cyanoacetate with 2-chloroethyl chloroformate. More recently, Konopelski obtained the keteneacetal from the KH and β-haloxydrin esters. These investigations prompted us to explore the possibility that the cyclopentadiene could undergo similar reaction and thereby facilitate the preparation of 2. To a mixture of sodium cyclopentadienide (10 mmol) and NaOH (10 mmol) in CH3CN (20 mL) was added 2-chloroethyl chloroformate (10 mmol) at 25°C and the resulting mixture was stirred for 1 h to produce the desired fulvene 2 in 32% yield, (entry 1, Table 1). To optimize the reaction yield, a series of homologous substrates and conditions were subjected to the reaction (Table 1). Reaction of the NaOH and other reactants under various conditions did not enhance the yields (entry 2-4). KOH was next examined as the base for the second-step cyclization reaction and found to produce a higher yield (50%, entry 5). However, an excess of KOH caused the product to decompose and subsequently produced lower yields (entries, 6, 7). Changes in the reaction solvent under the same conditions only slightly influenced the yield (entries 8-11).
Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting Cp (equiv, mL of solvent)$^a$</th>
<th>Base (equiv)</th>
<th>after the addition of chloroformate (temp, time)$^b$</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCp (1, 20)</td>
<td>NaOH (1)</td>
<td>(25°C, 1 h)</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>NaCp (1, 20)</td>
<td>NaOH (1)</td>
<td>(25°C, 1 h)</td>
<td>32$^c$</td>
</tr>
<tr>
<td>3</td>
<td>NaCp (1, 20)</td>
<td>NaOH (1)</td>
<td>(0°C, 7 h)</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>NaCp (1, 20, DME)</td>
<td>NaOH (1)</td>
<td>(0°C, 5 h)</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>NaCp (1, 20)</td>
<td>KOH (1)</td>
<td>(0°C, 5 h)</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>NaCp (1, 20)</td>
<td>KOH (2)</td>
<td>(0°C, 8 h)</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>NaCp (1, 20)</td>
<td>KOH (3)</td>
<td>(0°C, 8 h)</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>NaCp (1, 20, DME)</td>
<td>KOH (1)</td>
<td>(0°C, 5 h)</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>NaCp (1, 20, THF)</td>
<td>KOH (1)</td>
<td>(25°C, 4 h)</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>NaCp (1, 20)</td>
<td>KOH (1.1) in H$_2$O (5 mL)</td>
<td>(25°C, 2 h)</td>
<td>35</td>
</tr>
<tr>
<td>11</td>
<td>NaCp (1, 20)</td>
<td>KOH (1.1) in HO(CH$_2$)$_2$OH (5 mL)</td>
<td>(25°C, 4 h)</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>NaCp (1, 20, THF)</td>
<td>t-BuOK (1)</td>
<td>(25°C, 3 h)</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>NaCp (1, 20, THF)</td>
<td>KHMDS (1)</td>
<td>(25°C, 4 h)$^d$</td>
<td>55</td>
</tr>
<tr>
<td>14</td>
<td>NaCp (1, 20, THF)</td>
<td>NaHMDS (1)</td>
<td>(25°C, 4 h)$^d$</td>
<td>57</td>
</tr>
<tr>
<td>15</td>
<td>NaCp (2, 20)</td>
<td>0</td>
<td>(0°C, 4 h)</td>
<td>50</td>
</tr>
<tr>
<td>16</td>
<td>NaCp (1, 20)</td>
<td>NaCp (1)$^e$</td>
<td>(0°C, 4 h)</td>
<td>54</td>
</tr>
<tr>
<td>17</td>
<td>NaCp (1, 20)</td>
<td>NaCp (1)$^e$</td>
<td>(25°C, 1 h)</td>
<td>58</td>
</tr>
<tr>
<td>18</td>
<td>NaCp (1, 40)</td>
<td>NaCp (1)$^e$</td>
<td>(25°C, 1 h)</td>
<td>65</td>
</tr>
<tr>
<td>19</td>
<td>NaCp (1, 60)</td>
<td>NaCp (1)$^e$</td>
<td>(25°C, 1 h)</td>
<td>76</td>
</tr>
<tr>
<td>20</td>
<td>NaCp (1, 80)</td>
<td>NaCp (1)$^e$</td>
<td>(25°C, 1 h)</td>
<td>84</td>
</tr>
<tr>
<td>21</td>
<td>NaCp (1, 100)</td>
<td>NaCp (1)$^e$</td>
<td>(25°C, 1 h)</td>
<td>86</td>
</tr>
<tr>
<td>22</td>
<td>NaCp (2, 100)</td>
<td>0</td>
<td>(25°C, 1 h)</td>
<td>85</td>
</tr>
</tbody>
</table>

$^a$ CH$_3$CN was used as solvent unless otherwise indicated.

$^b$ 2-Chloroethyl chloroformate (10 mmol) was added at 0°C for 15 min.

$c$ Chloroformate was added at -30°C for 30 min.

$d$ No reaction was observed at 0°C for 4 h.

$^e$ The second equivalent of NaCp was added after the addition of chloroformate.
The reaction using other bases such as KHMDS and NaHMDS afforded higher yields (entries 13, 14). In contrast, the reaction with t-BuOK yielded no desired product (entry 12). On the other hand, sodium cyclopentadienide can also serve as a base in the second-step cyclization reaction. Adding two equivalents of sodium cyclopentadienide to the reaction mixture produced fulvene 2 in a reasonable yield (54%, entries 15, 16). To eliminate the possibility of polymerization in the cyclization step, dilute reaction conditions were then examined. According to those results, the reaction reached the highest yield (86%) in the concentration of 0.1 M (entries 17-21). Although a practical methodology for preparing fulvene 2 has been developed, a simpler method is necessary since the sodium cyclopentadienide must still be prepared or purchased at costly price. The second generation of this preparation was then examined (Table 2).

Two equivalents of potassium cyclopentadienide were generated in situ in the reaction of cyclopentadiene and KOH. The second equivalent of potassium cyclopentadienide functioned as a base in the cyclization step. Reactions under these conditions produced the fulvene 2 in moderate yields (22-25%, entries 1-3, table 2). We suspected that the incomplete formation of the potassium cyclopentadienide might be the cause of the low-yielding reaction. A concentrated solution (5 mL of CH₃CN) was then used to form potassium cyclopentadienide (4 M used, instead of 1 M). After the potassium cyclopentadienide was formed, the reaction was diluted back to the usual concentration by adding CH₃CN (15 mL) to the reaction mixture, followed by adding of 2-chloroethyl chloroformate (10 mmol) and stirring at 25°C for 1 h. A higher yield was observed via this procedure (57%, entry 4, Table 2). Consequently, many dilute conditions in the second step were examined to prevent the polymerization in the cyclization reaction. Similar to the
results in Table 1, the reaction reached the highest yield (82%) under the condition of 0.1 M (calculated by chloroformate, entries 5-7). Moreover, the second-step cyclization reaction is not a moisture sensitive reaction. A similar yield was observed after adding H₂O (1 mL) to the reaction mixture of chloroformate and potassium cyclopentadienide (75%, entry 8, Table 2).

Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting Cp (equiv, mL of CH₃CN)</th>
<th>Base used for the formation of Cp anion (equiv)²</th>
<th>CH₃CN added after the formation of Cp anion (mL)b</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cp (1, 20)</td>
<td>KOH (2)</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>Cp (2, 20)</td>
<td>KOH (2)</td>
<td>0</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>Cp (2, 20)</td>
<td>KOH (3)</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Cp (2, 5)</td>
<td>KOH (2)</td>
<td>15</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>Cp (2, 5)</td>
<td>KOH (2.5)</td>
<td>75</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>Cp (2, 5)</td>
<td>KOH (2.5)</td>
<td>95</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>Cp (2, 5)</td>
<td>KOH (2.5)</td>
<td>120</td>
<td>82</td>
</tr>
<tr>
<td>8</td>
<td>Cp (2, 3)</td>
<td>KOH (2.5)</td>
<td>120</td>
<td>78</td>
</tr>
<tr>
<td>9</td>
<td>Cp (2, 5)</td>
<td>KOH (2.5)</td>
<td>95</td>
<td>75⁵</td>
</tr>
</tbody>
</table>

² Potassium cyclopentadiene was formed at 25°C (1h).

b 2-Chloroethyl chloroformate (10 mmol) was added at 0°C for 15 min and the reaction was stirred at 25°C for 1h.

⁵ 1 mL of H₂O was added after the addition of chloroformate.

As the entries of Table 1 and 2 illustrate, reacting two equivalents of sodium cyclopentadienide or cyclopentadiene and KOH at 0.1 M produce the highest yield for the preparation of fulvene 2 (entry 21, Table 1; entry 6 Table 2). This
procedure for preparing 2 is characterized by a much higher overall yield and easy operation. The procedure also lies in fact that the cyclopentadiene and 2-chloroethyl chloroformate are both commercial available and low costs.\textsuperscript{12}

In summary, this work synthesizes 2-cyclopentadienyliden-1,3-dioxolane 2 by a relatively simple and efficient rout. The procedure should make fulvene 2 readily available as an important intermediate for organic synthesis.

**Experimental Section**

**2-Cyclopentadienyliden-1,3-dioxolane.** Method A: To a solution of sodium cyclopentadienide (10 mL, 2.0 M in THF, 20 mmol) in dry CH\textsubscript{3}CN (100 mL) was added dropwise 2-chloroethyl chloroformate (1.43 g, 10 mmol) over a period of 15 min at 0°C. The reaction mixture was stirred at 25°C for 1 h. The resulting solution was filtered through celite and the filtrate was concentrated \textit{in vacuo} to give the crude fulvene 2 as a brown solid. The compound was purified by flash column chromatography (Al\textsubscript{2}O\textsubscript{3}) with 20% EtOAc-hexane ($R_f = 0.50$ in 30% EtOAc-hexane) to give the fulvene 2 as a white solid (1.17 g, 86% yield).

Method B: To a solution of cyclopentadiene (1.32 g, 20 mmol) in dry CH\textsubscript{3}CN (5 mL) was added finely powdered KOH (1.4 g, 25 mmol) and the solution was stirred at 25 °C for 1h. CH\textsubscript{3}CN (95 mL) was then added to the reaction mixture. To this solution 2-chloroethyl chloroformate (1.43 g, 10 mmol) was added dropwise over a period of 15 min at 0°C. Then, the reaction mixture was stirred at 25°C for 1 h. The resulting solution was filtered through celite and the filtrate was concentrated \textit{in vacuo} to give the crude fulvene 2 as a brown solid. The compound was purified by flash column chromatography (Al\textsubscript{2}O\textsubscript{3}) with 20%
EtOAc-hexane to give the fulvene 2 as a white solid (1.12 g, 82% yield). IR (neat): 2968, 2880, 1750, 1467, 1261, 1183, 1090 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 6.61-6.63 (m, 2 H), 6.29-6.31 (m, 2 H), 4.55 (s, 4 H); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 163.88 (C), 123.80 (two C of CH), 118.14 (two C of CH), 98.41 (C), 67.42 (two C of CH\(_2\)); MS (m/z, relative intensity): 136 (M\(^+\), 50), 111 (10), 92 (100), 85 (55), 83 (85), 64 (23), 63 (28), 57 (55); exact mass calculated for C\(_8\)H\(_8\)O\(_2\) (M\(^+\)): 136.0524; found 136.0555. Anal. Calcd for C\(_8\)H\(_8\)O\(_2\): C, 70.59; H, 5.88. Found: C, 70.68; H, 5.98.

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**References and Notes:**


with BrCH₂CH₂Br, see: Gompper, R.; Kutter, E. Chem. Ber. 1965, 98, 2825. (c) Because of the increasing attention of this fulvene, the dithiolane 1 has been commercially available since 1996 (Aldrich Chemical Company).


The dioxolane 1 produced different chemoselectivities with dithiolane 2; Hong, B.-C.; Sun, S.-S., unpublished results.


Costs calculated using current Aldrich Chemical Company catalog price (1996-1997). For comparison, a mole of bis(cyclopentadienyl)nickel from Aldrich costs $1700; a mole of CF₃I gas from Aldrich cost $713.

No detailed procedure has been reported for the preparation of fulvene 2 in Scheme 2. However, the reaction is much more complicate and has a significantly lower overall yield than our methodology described (vide infra).


Costs calculated using current Aldrich Chemical Company catalog price (1996-1997). For comparison, 119 moles of cyclopentadiene (distilled from
dicyclopentadiene) costs $38; a mole of 2-chloro ethyl chloroformate costs $51.5.

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