Cycloaddition of 2-phenyl-3-ethoxycarbonyl-\(\Delta^2\)-pyrroline-4,5-dione with butadiene. Evidence of [1,3] sigmatropy for formation of the diels-alder product

Takehiro Sano and Yoshiyuke Tsuda

Showa College of Pharmaceutical Sciences, Setagaya-ku,
Tokyo-154, Japan

Thermal and photochemical cycloaddition of 2-phenyl-3-ethoxycarbonyl-\(\Delta^2\)-pyrroline-4,5-dione (1) with butadiene afforded the same 1,2-adduct (2) in regio- and stereoselective manner. At elevated temperature the 1,2-adduct (2) changed by an 1,3-sigmatropic shift into the normal Diels-Alder adduct (3). The easiness of sigmatropy was greatly influenced by the nature of N-substituents and decreased by the following order: H > Me > Ph. In case of N-phenyl derivative, the rearrangement was not observed.

Previously Tsuda and Isobe\(^2\) reported that 3-phenyl-\(\Delta^2\)-pyrroline-4,5-dione possessed a dienophile character and gave the normal Diels-Alder product in thermal reaction with butadiene. We present here cycloaddition reaction of 2-phenyl derivative with butadiene, which behaves quite differently.
Heating of 2-phenyl-3-ethoxycarbonyl-Δ²-pyrroline-4,5-dione (1a) with butadiene in CH₂Cl₂ or in DMF at 120° for 40 hr gave an 1:1 adduct in about 10% yield, which was unexpectedly the [2+2] cycloadduct (1,2-adduct) and identical with the photocycloadduct³ (2a) obtained (47%) by irradiation of 1a and butadiene in dimethoxyethane (-10°, 40 min.) with high pressure mercury lamp. The formation of 2a in the both photolytic and thermal reaction was highly regio- and stereoselective, no 1,4-adduct being found in the mixture. While heating of 1a and butadiene at 180° for 28 hr in CH₂Cl₂, the [4+2] cycloadduct (3a) was produced in 10% yield, the 1,2-adduct being not detected in this case. The 1,2- and 1,4-cycloadduct were easily characterized respectively by their spectral data as seen in Table I.

\[
\begin{align*}
\text{EtOOC} & \quad \text{H₂C} \text{H₂C} \text{H₂C} \text{H₂C} \\
\text{Ph} & \quad \text{R} \\
(1) & \quad \text{Δ}(120°) \quad \text{or hν} \\
\end{align*}
\]

\[
\begin{align*}
\text{H₂C} & \quad \text{COOEt} \\
\text{H₂C} & \quad \text{R} \\
(2) & \quad \Delta \\
\end{align*}
\]

\[
\begin{align*}
\text{H₂C} & \quad \text{COOEt} \\
\text{H₂C} & \quad \text{R} \\
(3) & \\
\end{align*}
\]

\[
\begin{align*}
\text{H₂C} & \quad \text{COOEt} \\
\text{H₂C} & \quad \text{R} \\
(4) & \\
\end{align*}
\]

\[
\begin{align*}
\text{H₂C} & \quad \text{COOEt} \\
\text{H₂C} & \quad \text{R} \\
(5) & \\
\end{align*}
\]

R: a=H, b=COCH₃, c=Me, d=Ph
Table I. Physical and Spectral Data of the Cycloadducts

<table>
<thead>
<tr>
<th>1,2-adduct m.p.</th>
<th>IR(Nujol) cm⁻¹</th>
<th>NMR(δ,ppm)</th>
<th>olefinic protons (3H)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>146-149°</td>
<td>1765, 1740, 1700</td>
<td>4.9 6.0</td>
</tr>
<tr>
<td>2b</td>
<td>146-148°</td>
<td>1775, 1760, 1740, 1717</td>
<td>5.0 6.0</td>
</tr>
<tr>
<td>2c</td>
<td>164-166°</td>
<td>1765, 1740</td>
<td>5.1 6.3</td>
</tr>
<tr>
<td>2d</td>
<td>199-201°</td>
<td>1765, 1741, 1725</td>
<td>5.2 6.5</td>
</tr>
<tr>
<td>4</td>
<td>193-195°</td>
<td>1772, 1741, 1720</td>
<td>5.2 6.5</td>
</tr>
<tr>
<td>5</td>
<td>180-183°</td>
<td>1762, 1742, 1725</td>
<td>4.9 5.5</td>
</tr>
<tr>
<td>1,4-adduct</td>
<td></td>
<td></td>
<td>olefinic protons</td>
</tr>
<tr>
<td>3a</td>
<td>228-230°</td>
<td>1780, 1755, 1730</td>
<td>6.03§</td>
</tr>
<tr>
<td>3b</td>
<td>164-166°</td>
<td>1780, 1740, 1720, 1700</td>
<td>5.97†</td>
</tr>
<tr>
<td>3c</td>
<td>158-160°</td>
<td>1765, 1740, 1720</td>
<td>6.02†</td>
</tr>
</tbody>
</table>

* Signal showed a typical splitting pattern of vinyl protons.
§ Signal appeared as diffused multiplets.
† Signal appeared as a broad singlet.

The regio- and stereochemistry of the vinyl group in 1,2-adduct (2) was elucidated from the analogy of the photocycloadduct (4) of N-4’-bromophenyl derivative with butadiene, whose structure has been determined by X-ray analysis. The chemical shifts and the splitting patterns due to the protons on the cyclobutane ring of 2a-2d were similar to those of 4 as shown in Table II.
Table II. NMR Spectra of 1,2-Adduct (δ, ppm)

<table>
<thead>
<tr>
<th>compound</th>
<th>H₁</th>
<th>H₂</th>
<th>H₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>2.50</td>
<td>3.07</td>
<td>3.30</td>
</tr>
<tr>
<td>2c</td>
<td>2.45</td>
<td>~π</td>
<td>3.20</td>
</tr>
<tr>
<td>2d</td>
<td>2.60</td>
<td>3.26</td>
<td>3.45</td>
</tr>
<tr>
<td>4</td>
<td>2.55</td>
<td>3.17</td>
<td>3.48</td>
</tr>
</tbody>
</table>

H₁ : Signals appeared as a pair of two quartets.
H₂ : The signal appeared as a quartet. The chemical shift given here indicates a half (doublet) of it, which appeared at upper field. The other half at lower-field is overlapped with signals of other protons.
H₃ : Signal appeared as a multiplet.
π : Signal is overlapped with N-Me signal.

On heating the compound (2a) at 180° for 6 hr in toluene it furnished quantitatively the 1,4-adduct (3a). This indicates that [4+2] adduct (3a) formed by the reaction of 1a with butadiene is not the initial product but was formed from the [2+2] adduct (2a) by [1,3] sigmatropic rearrangement with retention of the configuration at migrating carbon.

The yield of 2a and hence that of 3a were markedly improved by changing the solvent to acetic anhydride. Thus, by the reaction at 100° for 80 hr N-acetyl-1,2-adduct (2b) and at 160° for 8 hr N-acetyl-1,4-adduct (3b) were produced in 20% and 60% yields, respectively. Again 2b rearranged to 3b on heating at
160° for 10 hr in acetic anhydride. This marked improvement of
the yield by using acetic anhydride is not merely attributable
to the solvent effect of changing the polarity but is understood
by assuming the formation of an intermediate N-acetyl-\(\alpha\)-
pyrroline-4,5-dione (1b) whose electrophilicity at C2 is ap-
parently increasing compared to 1a. In fact, acetic anhydride
was not effective for N-methyl derivative (1c) which gave 1,2-
adduct (2c) (~10%) at 160° for 8 hr and 1,4-adduct (3c) (~10%)
at 180° for 24 hr by reaction with butadiene in either CH2Cl2
or acetic anhydride. The same 1,2-adduct (2c) was obtained in
30% yield by photo-cycloaddition and rearranged into 1,4-adduct
(3c) on heating at 180°. Photo-cycloaddition of N-phenyl deriv-
ative (1d) with butadiene gave two 1,2-cycloadducts (2d) (major)
and (5) (minor). The minor product (5) was elucidated as a
stereoisomer of 2d since its spectral data were very close to
those of 2d except that the NMR signal (δ, 4.31 m.) of the proton
with asterisk in 5 appeared at lower field by 0.86 ppm than that
of 2d. This indicated that the ethoxycarbonyl in 5 are in cis-
arrangement. Even heating above 200°, 2d did not rearranged
to the N-phenyl-1,4-cycloadduct (3d), but thermal decomposition
took place to give a complex mixture. The above evidence indi-
cates that the thermal [1,3]sigmatropy of (2)→(3) is greatly
influenced by the nature of N-substituent.

Ionic rearrangement (2)→(3) in the case of N-hydrogen deriv-
ative was also observed. Treatment of 2a with 5% hydrochloric
acid in methanol for 30 min. gave 3a in good yield. Neither
N-methyl nor N-phenyl derivatives rearranged into the corresponding 1,4-adduct.

REFERENCES


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