Supplementary Information

Regioisomeric Allene Dimer Formation by the Reaction of Tetraarylbutatrienes with Tetracyanoethene

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(1) Time dependent $^1$H-NMR spectra (in CDCl$_3$) of the reaction of tetraarylbutatriene 1b with TCNE.
(2) $^1$H-NMR and $^{13}$C-NMR spectra (in CDCl$_3$) of products.
\[ \text{Ar}^1 = p-\text{MeOC}_{6}\text{H}_{4} \quad \text{Ar}^2 = p-\text{MeC}_{6}\text{H}_{4} \]
\[
2b \quad Ar^1 = p-\text{MeOC}_6 H_4 \quad Ar^2 = p-\text{MeC}_6 H_4
\]
\[
\begin{align*}
2c & \quad \text{Ar}^1 = \text{p-MeOC}_2\text{H} \quad \text{Ar}^2 = \text{p-ClC}_6\text{H}_4 \\
\end{align*}
\]
\[ \text{Ar}^1 = \text{p-MeOC}_6\text{H}_4 \quad \text{Ar}^2 = \text{p-ClC}_6\text{H}_4 \]
6a

$\text{Ar} = p\text{-MeOC}_6\text{H}_4$  $\text{Ar} = p\text{-MeOC}_6\text{H}_4$  $R = \text{OMe}$
Ar\(^1\) = p-MeOC\(\_\)H\(_4\)  Ar\(^2\) = p-MeC\(\_\)H\(_4\)  R = Me

(No further purification was achieved by recrystallization or by preparative layer chromatography.)
S-14
(a) $^1$H-NMR spectra (in CDCl$_3$) of 2b' and 2c'.

From $^1$H-NMR spectra of crude product 2b (see the upper figure), three singlets (2.42, 3.88 and 3.89 ppm) derived from the methyl signals of the methylphenyl and methoxyphenyl groups are confirmed. In addition, two singlets (2.43, 3.86 ppm) are also appeared close to signals of 2b and the integrations of these two signals are equivalent each other. As compared with the methyl signals of the methoxyphenyl group of 2a and analogous compound 1 (see figure on the right), these signals are presumed to be due to 2b', which is a regioisomer of 2b. From integration of $^1$H-NMR spectra, the isomer 2b' was obtained in 1/6 of the yield of 2b.

Reference
$^1$H-NMR spectra of crude product of the reaction of 1c and TCNE (see the upper figure) showed that not only the methyl signals of the methoxyphenyl group of 2c (3.90 ppm) but also two singlets (3.86 and 3.87 ppm) were existed. One singlet 3.87 ppm is confirmed to be derived from material compound 1c (see S-5). Along with the case of 2b', the other singlet 3.86 ppm is assumed to be due to 2c' which is a regioisomer of 2c. From integration of $^1$H-NMR spectra, the isomer 2c' was obtained in 1/20 of the yield of 2c. In addition, the methyl signals of the methoxyphenyl group of 3c could be confirmed (See S-9).
(4) ESI-TOF-MS spectra of products.

**Calc. Mass** 605.2189  
**Formula** $C_{38}H_{29}N_4O_4^+$

**Calc. Mass** 571.2134  
**Formula** $C_{38}H_{27}N_4O_2^-$
$\text{Ar}_1 + \text{p-MeOC}_6\text{H}_4 = \text{p-ClC}_6\text{H}_4\text{Cl}$

$\text{R} = \text{Cl}$

1. $\text{Ar} = \text{p-MeOC}_6\text{H}_4$
2. $\text{Ar} = \text{p-ClC}_6\text{H}_4$
3. $\text{R} = \text{Cl}$

**Calc. Mass:** 611.1042
**Formula:** $\text{C}_{36}\text{H}_{21}\text{N}_4\text{O}_2\text{Cl}_2$

**Calc. Mass:** 606.2029
**Formula:** $\text{C}_{38}\text{H}_{28}\text{N}_3\text{O}_5^+$

**Calc. Mass:** 606.2029
**Formula:** $\text{C}_{38}\text{H}_{28}\text{N}_3\text{O}_5^+$

$\text{Ar} = \text{p-MeOC}_6\text{H}_4$

$\text{Ar} = \text{p-MeOC}_6\text{H}_4$

$\text{R} = \text{Cl}$

$\text{R} = \text{Cl}$
$9b$

$\text{Ar}^1 = p$-MeOC$_2$H$_4$  $\text{Ar}^2 = p$-MeC$_6$H$_4$

Calc. Mass  574.2131
Formula  $\text{C}_{20}\text{H}_{14}\text{N}_3\text{O}_3^+$

$9c$

$\text{Ar}^1 = p$-MeOC$_2$H$_4$  $\text{Ar}^2 = p$-ClC$_6$H$_4$

Calc. Mass  614.1038
Formula  $\text{C}_{36}\text{H}_{22}\text{N}_3\text{O}_3\text{Cl}_2^+$
(5) UPLC-MS analyses of 6b and 6c

Column: 1.7 μm ACQUITY UPLC BEH C18, 50 × 2.1 mm
Injection volume: 3 ppm × 7 μl
Column temperature: 40°C

Gradient separations

<table>
<thead>
<tr>
<th>Time</th>
<th>Flow [ml/min]</th>
<th>0.1% Formic acid H2O [%]</th>
<th>0.1% Formic acid CH3CN [%]</th>
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</tr>
<tr>
<td>10 min</td>
<td>0.1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>10.1 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>11 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

Main product 6b
Regioisomer of 6b?

Calc. Mass 573.2291
Formula C38H29N4O2+ 
Column: 1.7 μm ACQUITY UPLC BEH C\textsubscript{18}, 50 × 2.1 mm
Injection volume: 3 ppm × 7 μl
Column temperature: 40°C

Gradient separations

<table>
<thead>
<tr>
<th>Time</th>
<th>Flow [ml/min]</th>
<th>0.1% Formic acid H\textsubscript{2}O [%]</th>
<th>0.1% Formic acid CH\textsubscript{3}CN [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
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</tr>
<tr>
<td>11 min</td>
<td>0.1</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

Calc. Mass: 611.1042
Formula: C\textsubscript{36}H\textsubscript{21}N\textsubscript{4}O\textsubscript{2}Cl\textsubscript{2}
(6) Crystal structures of products.

**1b** (CCDC 937964)
Selected bond length (Å): C1-C2 1.346(3), C2-C3 1.248(3), C3-C4 1.334(3)

**2b** (CCDC 937945)

**2c** (CCDC 937946)

**9b** (CCDC 958310)

**9c** (CCDC 937949)