Usual and unusual reactions of cyclohexane-1,2-dione with aryl azides and amines: a structural corrigendum

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[1] General Information

**IR spectra** were measured on a FT-IR Spectrometer *Nicolet iS5* from THERMO FISCHER SCIENTIFIC. Spectra were measured in suitable organic solvents and are reported in cm\(^{-1}\) in decreasing order of wavenumber (\(\bar{\nu}\)).

**NMR spectra** were measured on a *UNITY INOVA 400* FT spectrometer from VARIAN. \(^1\)H NMR spectra were measured at 400 MHz and \(^{13}\)C NMR at 100 MHz. NMR signals were referenced to TMS (\(\delta = 0\)) or solvent signals and recalculated relative to TMS. 2D NMR methods, such as gCOSY gHSQCAD, CIGAR etc. were used for assignment of signals, when necessary. Multiplicities of the signals are reported using the standard notations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. s = broad singlet, etc.

**Mass spectra** were obtained from *micrOTOF QII* spectrometer from BRUKER utilizing electrospray-ionisation technique (ESI).

**Quantitative elemental analyses** were performed on a *Vario Micro Tube* from ELEMENTAR ANALYSENSYSTEME GMBH HANAU.

**Thin layer chromatography** was performed using *Macherey-Nagel Polygram SIL G/UV\(_{254}\) foils*.

**Flash chromatography** was performed with Silica gel 60 M (particle-size 0.04–0.063 mm) as the stationary phase from the company *Macherey-Nagel*.

**Melting points** were recorded on a *Pentakon Dresden Boetius* apparatus and are uncorrected.
[2] Synthesis and characterisation of triazole 3e:

**General Procedure:** To a solution of cyclohexane-1,2-dione (0.3 mmol) and the corresponding aryl azide (0.6 mmol) in THF (1.0 mL), was added pyrrolidine (0.3 mmol) and the mixture was stirred for 48 h at RT. Purification by silica-gel flash chromatography yields the desired products 3b and 3e.

<table>
<thead>
<tr>
<th>Supposed product 1e from cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methylbenzene</th>
<th>Product 3e from cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow oil; yield (76%).</td>
<td>Yellow oil; yield (47%); purified by flash chromatography (Rf = 0.45; SiO2; Et2O:n-pentane 1:1).</td>
</tr>
<tr>
<td><strong>1H NMR (500 MHz, CDCl3):</strong> δ = 1.45–1.50 (m, 1H), 1.63–1.76 (m, 6H), 2.19–2.32 (m, 6H), 2.40–2.44 (m, 2H), 2.61–2.64 (m, 2H), 4.81–4.83 (m, 1H), 7.09 (d, J = 10 Hz, 2H), 7.39 (d, J = 10 Hz, 2H).</td>
<td><strong>1H NMR (400 MHz, CDCl3):</strong> δ = 1.41–1.53 (m, 1H), 1.59–1.79 (m, 6H), 2.18–2.37 (m, 3H), 2.28 (s, 3H), 2.39–2.44 (m, 2H), 2.61–2.66 (m, 2H), 4.81 (m, 1H), 7.08 (d, J = 8.8 Hz), 7.39 (d, J = 8.8 Hz, 2H).</td>
</tr>
<tr>
<td>13C NMR (125 MHz, CDCl3): δ = 17.1, 20.7, 24.0, 26.3, 37.3, 45.8, 81.0, 82.9, 116.7, 129.7, 133.6, 137.2, 204.2</td>
<td>13C NMR (100 MHz, CDCl3): δ = 17.07 (t, CHCH3), 20.68 (q, CH3), 23.94 (t, NCH2CH3), 2 × CH3, 26.27 (t, COCH2CH3), 37.26 (t, COCH3), 45.71 (t, NCH2), 2 × CH3, 80.95 (d, CH), 82.82 (s, NCN), 116.66 (d, C-2'), 129.69 (d, C-3'), 133.54 (s, Cquat), 137.16 (s, Cquat), 204.15 (s, C=O).</td>
</tr>
<tr>
<td>IR: N.A.</td>
<td>IR (CDCl3, cm⁻¹): 1722 (C=O).</td>
</tr>
</tbody>
</table>

HR-MS (ESI): m/z calcd. for C17H23N4O2 [M⁺] 299.1866; found: 299.1863

HR-MS (ESI): m/z calcd. for C17H24N4O2 [M + H]⁺ 299.1866; found: 299.1849

The structure assignment for 3e has been further confirmed by 1D NOESY and gHSQCAD NMR analytical techniques.

Scheme 1. Results from the 1D NOESY experiment (3e).
**Three** Synthesis and characterisation of amide 4e:

**General Procedure:** To a solution of cyclohexane-1,2-dione (0.3 mmol) and the corresponding aryl azide (1.2 mmol) in CHCl$_3$ (1.1 mL), was added diethylamine (0.3 mmol) and the mixture was stirred for 48 h at RT. Purification by silica-gel flash chromatography yields the desired products 4b and 4e.

<table>
<thead>
<tr>
<th>Supposed product 2e$^{8a}$ from cyclohexane-1,2-dione, diethylamine and 1-azido-4-methylbenzene</th>
<th>Product 4e from cyclohexane-1,2-dione, diethylamine and 1-azido-4-methylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow solid. mp N.A.</td>
<td>Yellow solid; yield (53%); mp 127 °C; purified by flash chromatography ($R_f$ = 0.42; SiO$_2$: Et$_2$O).</td>
</tr>
<tr>
<td>$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.83$-$1.91$ (m, 1H), 2.06-$2.11$ (m, 1H), 2.30 (s, 3H), 2.32-$2.47$ (m, 4H), 3.13 (t, $J = 10$ Hz, 1H), 7.11 (d, $J = 10$ Hz, 2H), 7.42 (d, $J = 10$ Hz, 2H), 8.65 (br., 1H).</td>
<td>$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.77$-$1.89$ (m, 1H), 1.99-$2.14$ (m, 1H), 2.26-$2.46$ (m, 4H), 2.30 (s, 3H), 3.12 (t, $J = 9.2$ Hz), 7.10 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz), 8.70 (br. s, 1H, NH).</td>
</tr>
<tr>
<td>$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 20.2$, 20.8, 25.7, 39.1, 54.6, 119.9, 129.4, 133.9, 135.1, 164.3, 217.0</td>
<td>$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 20.14$ (t, CH$_3$), 20.78 (q, CH$_3$), 25.67 (t, CH$<em>3$), 38.98 (t, CH$<em>3$), 54.58 (d, CH), 119.75 (d, C-2' or C-3'), 129.33 (d, C-2' or C-3'), 133.75 (s, C$</em>{quat}$), 135.07 (s, C$</em>{quat}$), 164.41 (s, CONH), 216.87 (C=O).</td>
</tr>
<tr>
<td>Anal. calcd. for N.A.</td>
<td>Anal. calcd. for C$<em>{13}$H$</em>{16}$N$_2$O: C 71.87, H 6.96, N 6.45; found: C 70.99, H 7.04, N 6.27</td>
</tr>
<tr>
<td>IR: N.A.</td>
<td>IR (CHCl$_3$, cm$^{-1}$): 1728 (C=O), 1681 (CONH), 3341 (NH).</td>
</tr>
<tr>
<td>HR-MS (ESI): m/z calcd. for C$<em>{13}$H$</em>{18}$N$_3$O$_2$ [M]$^+$ 246.1243; found: 246.1246</td>
<td>HR-MS (ESI): m/z calcd. for C$<em>{13}$H$</em>{18}$N$<em>3$O$<em>2$ [M + H]$^+$ 218.1176; found: 218.1149; for C$</em>{13}$H$</em>{15}$NNaO$_2$ [M + Na]$^+$ 240.0995; found: 240.0970</td>
</tr>
</tbody>
</table>

*Note:* This molecule was also prepared by a known analogous method$^{15b}$ for comparison. The spectra (pages 25–26) match perfectly with the above data.
[4] NMR and IR spectra
BANDENTABELLE:

Spektrum: Subtraktionsergebnis: NJC1
Bereich: 4000,00 400,00
Absoluter Schwellwert: 91,092
Empfindlichkeit: 50

Bandenlabeled:
Position: 738,51 Intensität: 43,237
Position: 742,36 Intensität: 43,558
Position: 747,09 Intensität: 43,364
Position: 754,34 Intensität: 45,442
Position: 773,50 Intensität: 46,032
Position: 777,52 Intensität: 46,277
Position: 788,55 Intensität: 49,875
$^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)
Subtraktionsergebnis: ArMetriazole

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BANDENTABELLE:

Spektrum: Subtraktionsergebnis: ArMetriazole
Bereich: 4000,00 400,00
Absoluter Schwellwert: 44,880
Empfindlichkeit: 50

Bandentabelle:

Position: 647,85  Intensität: 35,376
Position: 762,47  Intensität: 13,170
Position: 817,07  Intensität: 41,489
Position: 906,56  Intensität: 19,500
Position: 931,16   Intensität: 42,928
Position: 1062,08 Intensität: 38,131
Position: 1131,24 Intensität: 41,693
$^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)
BANDENTABELLE:

Spektrum: Subtraktionsergebnis:ArOMesubst
Bereich: 4000,00 400,00
Absoluter Schwellwert: 76,689
Empfindlichkeit: 50
Bandentabelle:

Position: 626,85 Intensität: 62,314
Position: 665,84 Intensität: 3,364
Position: 672,49 Intensität: 3,782
Position: 724,02 Intensität: 3,103
Position: 782,19 Intensität: 5,609
Position: 791,25 Intensität: 3,423
Position: 827,80 Intensität: 45,279
$^1$H NMR (CDCl$_3$)
BANDENTABELLE:
Spektrum: Subtraktionsergebnis:ArMesubst
Bereich: 4000,00  400,00
Absoluter Schwellwert: 77,082
Empfindlichkeit: 50
Bandentabelle:
Position: 502,75  Intensität: 73,503
Position: 626,60  Intensität: 62,631
Position: 665,92  Intensität: 3,359
Position: 672,43  Intensität: 3,624
Position: 724,14  Intensität: 3,036
Position: 743,70  Intensität: 3,187
Position: 791,16  Intensität: 3,424
$^1$H NMR (CDCl$_3$)
4e prepared from known method