Supporting Information

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The Exciting Chemistry of Tetraazidomethane**

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Experimental procedure

Safety instructions: Tetraazidomethane (1) is extremely dangerous as a pure substance. It can explode at any time – without a recognizable reason. Less than a drop of this compound isolated by gas chromatography is able to destroy not only the glass trap but also the Dewar vacuum flask of the cooling bath completely. Therefore, the isolated substance should only be diluted by vapor deposition of a solvent behind a safety shield but not by taking manual measures (pipette, syringe). However, solutions of 1 can also lead to an explosion after mechanical stress (swivel closure) or after evaporating of a volatile solvent, for example, in a pipette. Finally, it should be considered that 3, 5, and 7 are also explosive azides.

Tetraazidomethane (1) from 2h: Sodium azide (7.50 g, 115 mmol) was given to a solution of freshly distilled trichloroacetonitrile (2h, 2.50 g, 17.3 mmol) in acetonitrile (150 mL). The suspension was stirred at 50°C for 18 h and then diluted with water (100 mL) after cooling and removal of insoluble matter. The aqueous phase was extracted with n-pentane (3 x 70 mL), and the combined organic layers were washed with water (3 x 100 mL) and dried over MgSO₄. The solvent was removed in vacuo to give a residue (ca. 20–30 mL, caution, safety screen), which was filtered. The filtrate could be used for reactions of 1 or for purification of 1 by preparative gas chromatography. Alternatively, it could be utilised for NMR spectroscopy after addition of CD₃CN (3 mL) and evaporation of the solvent in vacuo to yield a volume of 1–2 mL. Compound 1 could be analysed by gas chromatography using capillary columns, 30 m, 80°C (methyl phenyl silicone, retention time 7.5 min; polyethylene glycol, retention time 6.5 min).
Figure S1: $^{15}$N NMR spectrum after the reaction of 1 with Na$^+$ $^{15}$N$_3^-$ in CD$_3$CN + H$_2$O (2 vol%) + DMSO (5 vol%), formation of $^{15}$N-1 and $^{15}$N-5.

Figure S2: $^{15}$N NMR spectrum after the reaction of 3a in CD$_3$CN with a substoichiometric amount of Na$^+$ $^{15}$N$_3^-$, formation of $^{15}$N-1 and $^{15}$N-3a.
**Table S1:** Selected physical data of the compounds 4a,b, 6, 8, 9a,b, 10a,b as well as the mono-oxide of 1,2-bis(diphenylphosphino)ethene (for comparison with the data of 8) and diazido(diphenoxy)methane.[a]

4a: Colorless crystals, m.p. 85–87°C; IR (CDCl₃): ν = 2941 cm⁻¹, 2857, 2138 (N₃); ¹H NMR (CDCl₃): δ = 1.47 (br. s, 12H), 1.61 (br. s, 6H), 1.76–1.79 (m, 6H), 2.45 (br. s, 6H), 2.93–2.96 (m, 6H); ¹³C NMR (CDCl₃): δ = 21.4 (t), 24.5 (t), 24.7 (t), 25.9 (t), 26.1 (t), 27.9 (t), 96.4 (s), 135.9 (s), 147.5 (s); C,H,N analysis (%): calcd for C₂₅H₃₆N₁₂ (504.63): C 59.50, H 7.19, N 33.31; found C 59.71, H 7.12, N 31.95.

4b: Colorless crystals, m.p. 218°C; IR (CDCl₃): ν = 2935 cm⁻¹, 2859; ¹H NMR (CDCl₃): δ = 1.29–1.82 (m, 36H), 2.37–2.47 (m, 4H), 2.93–2.99 (m, 8H); ¹³C NMR (CDCl₃): δ = 22.8 (t), 24.2 (t), 24.4 (t), 25.2 (t), 25.9 (t), 27.0 (t), 95.5 (s), 137.8 (s), 147.2 (s); MS (ESI) m/z (%) = 651.5 (100) [M + K]⁺; C,H,N analysis (%): calcd for C₃₃H₄₈N₁₂ (612.81): C 64.68, H 7.89, N 27.43; found C 64.63, H 7.87, N 27.30.

6: Colorless crystals, m.p. 192–194°C; IR (CDCl₃): ν = 2179 cm⁻¹ (CN); ¹H NMR (CDCl₃): δ = 7.47–7.52 (m, 6H), 7.59–7.66 (m, 9H); ¹³C NMR (CDCl₃): δ = 118.6 (s), 126.4 (d, JₚC = 97.7 Hz, i-Ph), 129.0 (d, JₚC = 12.9 Hz, m-Ph), 132.3 (d, JₚC = 10.4 Hz, o-Ph), 133.2 (d, JₚC = 2.8 Hz, p-Ph).

8: Colorless oil; IR (CDCl₃): ν = 2176 cm⁻¹ (CN); ¹H NMR (CDCl₃): δ = 2.25–2.31 (m, 2H), 2.40–2.49 (m, 2H), 7.33–7.34 (m, 10H), 7.47–7.52 (m, 4H), 7.59–7.64 (m, 6H); ¹³C NMR (CDCl₃): δ = 19.0 (dd, JₚC = 16.9 Hz, JₚC = 5.2 Hz, CH₂P), 24.2 (dd, JₚC = 67.5 Hz, JₚC = 18.9 Hz, CH₂P=N), 118.5 (s), 126.2 (d, JₚC = 97.7 Hz, i-Ph), 128.7 (d, JₚC = 6.7 Hz, m-Ph), 129.2–129.4 (several signals, m-Ph and p-Ph), 131.2 (d, JₚC = 10.1 Hz, o-Ph), 132.7 (d, JₚC = 18.9 Hz, o-Ph), 133.3 (d, JₚC = 2.7 Hz, p-Ph), 136.4 (d, JₚC = 13.2 Hz, i-Ph); ³¹P NMR (CDCl₃): δ = −12.1 (d, JₚP = 48.1 Hz), 29.6 (d, JₚP = 48.1 Hz); MS (ESI) m/z (%) = 439.1 (100) [M + H]⁺; HR-MS (ESI) m/z = 439.1501 [calcd 439.1488].

9a: White solid, m.p. 183–185°C; IR (CDCl₃): ν = 3414 cm⁻¹ (NH), 1585 (N–C=N); ¹H NMR (CDCl₃): δ = 0.99–1.03 (m, 2H, endo-H-5 (norbornene) and endo-H-6 (norbornene)), 1.35–1.37 (m, 2H, nortricyclane), 1.44 (m, 1H, nortricyclane), 1.49–1.52 (m, 2H,
nortricyclane), 1.57–1.61 (m, 2H, nortricyclane), 1.85–1.89 (m, 2H, exo-H-5 (norbornene) and exo-H-6 (norbornene)), 2.29 (m, 1H, H-4 (nortricyclane)), 2.94 (m, 1H, H-1 (norbornene) or H-4 (norbornene)), 2.97 (m, 1H, H-1 (norbornene) or H-4 (norbornene)), 3.90 (d, $^3J = 9.6$ Hz, 1H, H-7 (norbornene)), 4.08 (m, 1H, H-3 (nortricyclane)), 4.78 (d, $^3J = 9.3$ Hz, NH), 6.07–6.08 (m, 2H, H-2 (norbornene) and H-3 (norbornene)); $^{13}$C NMR (CDCl$_3$): $\delta = 11.4$ (d, nortricyclane), 12.3 (d, nortricyclane) and H-3 (norbornene), 13.0 (d, nortricyclane), 22.8 (t, C-5 (norbornene) or C-6 (norbornene)), 22.8, (t, C-5 (norbornene) or C-6 (norbornene)), 29.3 (t, nortricyclane), 31.1 (t, nortricyclane), 34.7 (d, C-4 (nortricyclane)), 45.7 (d, 2C, C-1 (norbornene) and C-4 (norbornene)), 62.1 (d, C-3 (nortricyclane)), 70.6 (d, C-7 (norbornene)), 132.5 (d, C-2 (norbornene) or C-3 (norbornene)), 132.8 (d, C-2 (norbornene) or C-3 (norbornene)), 155.4 (s, C-5 (tetrazole)); MS (ESI) $m/z$ (%) = 308.1 (100) [M + K]$^+$, 577.3 (48) [2M + K]$^+$; C,H,N analysis (%): calcd for C$_{15}$H$_{19}$N$_5$ (269.34): C 66.89, H 7.11, N 26.00; found C 66.52, H 7.42, N 25.72.

9b: White solid, m.p. 220–222°C; IR (CDCl$_3$): $\tilde{\nu} = 3440$ cm$^{-1}$ (NH), 1587 (N=C=N); $^1$H NMR (CDCl$_3$): $\delta = 1.19$–1.69 (m, 14H), 2.23 (m, 1H, H-4'), 2.36 (m, 1H, H-4), 3.79 (d, $^3J = 6.6$ Hz, 1H, H-3'), 4.10 (m, 1H, H-3), 4.38 (d, $^3J = 6.6$ Hz, 1H, NH); $^{13}$C NMR (CDCl$_3$): $\delta = 10.6$ (d), 11.7 (d), 12.4 (d), 12.5 (d), 13.2 (d), 15.0 (d), 29.5 (t), 29.7 (t), 31.3 (t), 31.5 (t), 33.4 (d, C-4'), 34.9 (d, C-4), 59.8 (d, C-3'), 62.3 (d, C-3), 154.9 (s, C-5 (tetrazole)); MS (ESI) $m/z$ (%) = 308.1 (42) [M + K]$^+$, 578.2 (100) [2M + K]$^+$; HR-MS (ESI) $m/z = 308.1293$ [calcd 308.1272].

10a: Yellow crystals, unstable compound, m.p. >320°C (decomp.); IR (CDCl$_3$): $\tilde{\nu} = 2104$ cm$^{-1}$ (N$_3$); $^1$H NMR (CDCl$_3$): $\delta = 1.31$ (d, $^3J = 8.7$ Hz, 1H, H-8 (norbornene)), 1.54 (d, $^2J = 11.8$ Hz, 1H, H-7 syn next to C-5 (nortricyclane)), 1.58 (d, $^2J = 11.8$ Hz, 1H, H-7 syn next to C-3 (nortricyclane)), 1.68 (m, 1H), 1.79 (m, 1H), 1.87 (d, $^2J = 8.7$ Hz, 1H, H-8 (norbornene)), 2.05 (m, 1H), 2.53 (br. s, 1H, H-4 (nortricyclane)), 3.09 (d, $^3J = 5.8$ Hz, 1H, H-2 (norbornene) or H-4 (norbornene)), 3.13 (d, $^3J = 5.8$ Hz, 1H, H-2 (norbornene) or H-4 (norbornene)), 3.14–3.16 (m, 2H, H-1 (norbornene) and H-5 (norbornene)), 3.92 (m, 1H, H-5 (nortricyclane)), 4.74 (m, 1H, H-3 (nortricyclane)), 6.42–6.43 (m, 2H, H-6 (norbornene) and H-7 (norbornene)); $^{13}$C NMR (CDCl$_3$): $\delta = 14.3$ (d, nortricyclane), 14.4 (d, nortricyclane), 16.2 (d, nortricyclane), 28.2 (t, C-7 (nortricyclane)), 38.4 (d, C-4 (nortricyclane)), 41.2 (t, C-8 (norbornene)), 42.4 (d, C-1 (norbornene) or C-5 (norbornene)), 42.5 (d, C-1 (norbornene) or C-5 (norbornene)), 50.0 (d, C-2 (norbornene) or C-4 (norbornene)), 50.2 (d, C-2 (norbornene))
or C-4 (norbornene)), 60.1 (d, C-3 (nortricyclane)), 66.4 (d, C-5 (nortricyclane)), 139.7 (d, C-6 (norbornene) or C-7 (norbornene)), 139.7 (d, C-6 (norbornene) or C-7 (norbornene)), 159.0 (s, C-5 (tetrazole)); MS (ESI) \(m/z\) (%) = 347.1 (100) [M + K]⁺, 655.2 (43) [2M + K]⁺; HR-MS (ESI); \(m/z\) = 347.1192 [calcd 347.1130].

10b: Colorless oil; IR (CCl₄): \(\tilde{\nu} = 2103\ \text{cm}^{-1}\) (N₃), 1522 (N–C=N); ¹H NMR (CDCl₃): \(\delta = 1.51\) (d, \(J = 11.7\ \text{Hz}\), 1H, H-7 \text{syn}\) next to C-5 (nortricyclane)), 1.62 (d, \(J = 11.7\ \text{Hz}\), 1H, H-7 \text{syn}\) next to C-3 (nortricyclane)), 1.65–1.66 (m, 2H, H-7 (homoquadricyclane)), 1.69 (m, 1H, H-6 (nortricyclane)), 1.81 (m, 1H, H-1 (nortricyclane)), 2.00 (m, 1H, H-2 (nortricyclane)), 2.08–2.09 (m, 2H, H-1 and H-2 (homoquadricyclane)), 2.32 (m, 1H, H-8 (homoquadricyclane)), 2.35 (m, 1H, H-4 (nortricyclane)), 2.80 (m, 1H, H-6 (homoquadricyclane)), 3.91 (m, 1H, H-5 (nortricyclane)), 4.48–4.50 (m, 2H, H-3 and H-5 (homoquadricyclane)), 4.51 (m, 1H, H-3 (nortricyclane)); ¹³C NMR (CDCl₃): \(\delta = 14.5\) (d, C-1 (nortricyclane)), 14.9 (d, C-2 (nortricyclane)), 16.1 (d, C-6 (nortricyclane)), 24.0 (d, C-1 or C-2 (homoquadricyclane)), 24.1 (d, C-1 or C-2 (homoquadricyclane)), 28.2 (t, C-7 (nortricyclane)), 31.3 (t, C-7 (homoquadricyclane)), 33.8 (d, C-8 (homoquadricyclane)), 38.5 (d, C-4 (nortricyclane)), 45.0 (d, C-6 (homoquadricyclane)), 59.8 (d, C-3 (nortricyclane)), 66.5 (d, C-5 (nortricyclane)), 70.5 (d, C-3 or C-5 (homoquadricyclane)), 71.2 (d, C-3 or C-5 (homoquadricyclane)), 158.3 (s, C-5 (tetrazole)); MS (ESI) \(m/z\) (%) = 346.9 (100) [M + K]⁺, 654.9 (20) [2M + K]⁺; HR-MS (ESI) \(m/z\) = 347.1163 [calcd 347.1130].

Ph₂P(O)CH₂CH₂PPh₂: ¹H NMR (CDCl₃): \(\delta = 2.26–2.30\) (m, 4H), 7.29–7.37 (m, 10H), 7.40–7.47 (m, 4H), 7.47–7.51 (m, 2H), 7.59–7.65 (m, 4H); ¹³C NMR (CDCl₃): \(\delta = 19.1\) (dd, \(J_{PC} = 15.3\ \text{Hz}\), 2\(J_{PC} = 4.3\ \text{Hz}\), CH₂P), 25.8 (dd, \(J_{PC} = 69.6\ \text{Hz}\), 2\(J_{PC} = 16.6\ \text{Hz}\), CH₂P=O), 128.5–128.9 (several signals, \(m\)-Ph und \(p\)-Ph), 130.7 (d, \(J_{PC} = 10.1\ \text{Hz}\), \(o\)-Ph), 131.8 (d, \(J_{PC} = 2.7\ \text{Hz}, p\)-Ph), 132.2 (d, \(J_{PC} = 98.6\ \text{Hz}\), \(i\)-Ph), 132.7 (d, \(J_{PC} = 18.5\ \text{Hz}\), \(o\)-Ph), 137.2 (d, \(J_{PC} = 13.4\ \text{Hz}, i\)-Ph); ³¹P NMR (CDCl₃): \(\delta = -11.6\) (d, \(J = 48.9\ \text{Hz}\)), 33.3 (d, \(J = 48.9\ \text{Hz}\)); MS (ESI) \(m/z\) (%) = 415.1 (100) [M + H]⁺.

(PhO)₂C(N₃)₂: Colorless liquid; IR (CDCl₃): \(\tilde{\nu} = 2139\ \text{cm}^{-1}\) (N₃), 1593 (Ph), 1491 (Ph), 1408 (Ph); ¹H NMR (CDCl₃): \(\delta = 7.20–7.46\) (m). ¹³C NMR (CDCl₃): \(\delta = 114.16\) (s, C-N₃), 120.92 (d), 125.27 (d), 129.47 (d), 151.82 (s).
[a] $^1$H NMR: 400 MHz, $^{13}$C NMR: 100.6 MHz, $^{31}$P NMR: 162 MHz. The assignments of NMR signals were performed with the help of $^1$H,$^1$H double resonance and $^1$H NMR NOE experiments, $^1$H,$^1$H (COSY) and $^{13}$C,$^1$H shift correlations, DEPT135 and GATED experiments with utilization of $^1$J($^{13}$C,$^1$H).


[c] This compound was treated with cyclooctyne, and the resulting triazole derivative was analysed to determine the number of azido groups.

Table S2: Selected $^1$H NMR and $^{13}$C NMR data of 10b and the known[a] compounds 15 and 16 in order to get evidence for the tetracyclic part of 10b.

<table>
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<th>Position</th>
<th>$^1$H NMR δ values (ppm)</th>
<th>$^{13}$C NMR δ values (ppm)</th>
<th>$^1$J($^{13}$C,$^1$H) (Hz)</th>
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<td>15</td>
<td>16</td>
<td>10b</td>
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<td>5</td>
<td>2.32</td>
<td>2.05–2.45</td>
<td>2.29</td>
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</table>

Scheme S1: Reaction mechanism to explain the formation of 6 from 1 and PPh₃.

Scheme S2: Alternative reaction mechanism to explain the products 9a and 9b; the simultaneousness and the order of the single steps are arbitrary.
Scheme S3: Reaction mechanism to explain the formation of 10a and 10b; the simultaneousness and the order of the single steps are arbitrary.