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Mannich functionalization of $C_{59}N$

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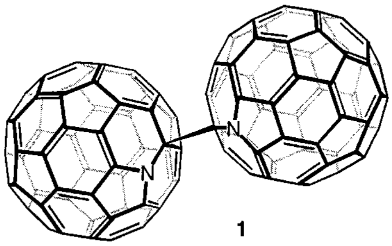
The thermal treatment of the heterofullerene dimer $(C_{59}N)_2$ with ketones and aldehydes in the presence of TsOH and air leads to Mannich-type functionalized heterofullerenes $RC_{59}N$.

We have shown recently[1] that arylated heterofullerenes $ArC_{59}N$ are easily accessible in yields up to 90% by the treatment of $(C_{59}N)_2$ **1**[2–5] with an electron-rich aromatic in the presence of TsOH and air. The proposed mechanism of this reaction involves an electrophilic aromatic substitution by $C_{59}N^+$, which is presumed to be formed *via* homolysis of the dimer, followed by oxidation of the $C_{59}N$ radical. The oxidation is a critical step, since running the reaction under an argon atmosphere did not yield arylated products. Here we report on the facile formation of the Mannich bases $RC_{59}N$ [R = CH(R′)COR″], obtained by the analogous treatment of **1** using enolizable aldehydes, ketones and 1,3-diketones as nucleophiles.



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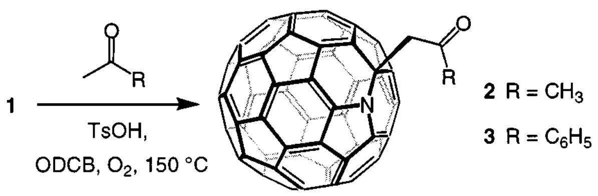
Mannich bases **2** and **3** were obtained in almost quantitative yield by the treatment of **1** in 1,2-dichlorobenzene with 20 equiv. of acetone or acetophenone and 40 equiv. of TsOH at 150 °C in a constant stream of air (Scheme 1). After 15 min the conversion was completed. The isolation of the products was achieved by flash chromatography on silica gel using toluene as mobile phase, where **2** and **3** elute as the least polar olive green coloured fraction.

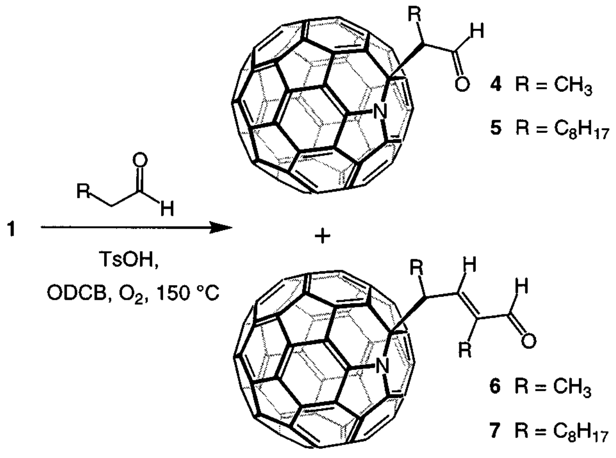
The complete structural characterization of **2** and **3** was carried out by ^1H NMR, ^{13}C NMR, UV–VIS and FT-IR spectroscopy as well as by mass spectrometry.† The ^1H NMR spectrum of **2**, for example, shows singlets for the methylene and the methyl groups at δ 4.91 and 2.79. The ^{13}C NMR spectrum clearly proves C_s symmetry, showing the 30 expected fullerene resonances in the sp^2 region between δ 155 and 123. The methylene group and the methyl group resonate at δ 53.84 and 30.90, respectively. The signal at δ 78.37 is due to the resonance of the sp^3 C-atom of the fullerene skeleton. The carbonyl C-atom resonates at δ 201.80. Except for the resonances of the addends the ^{13}C NMR spectrum of **3** is qualitatively the same. The UV–VIS spectra of the olive green solutions of **2** and **3**, with the most intensive absorptions located at 257, 320, 445, 589 and 724 nm, display the typical fingerprint for this type of heterofullerene derivatives.[1–5] The FT-IR spectra of **2** and **3** show the typical characteristics of fullerene derivatives (monoadducts), especially the absorptions in the fingerprint region between 480 and 590 cm^{-1}, with the strongest peak at about 524 cm^{-1}. The absorptions at 1729 (**2**) and 1692 cm^{-1} (**3**) are due to the C=O vibrations. EI mass spectrometry shows the M$^+$ peak of each compound together with a strong fragmentation peak at *m/z* 722 for $C_{59}N^+$.

The treatment of **1** with aldehydes like propanal and decanal under the same experimental conditions led also to complete conversion and the formation of the Mannich bases **4** and **5** respectively (Scheme 2). However, in these cases the aldol condensation products **6** and **7** are formed simultaneously. The amount of condensation products **6** and **7** increases with increasing reaction time, indicating that the condensation step proceeds with the initially formed heterofullerene derivatives **4** and **5**. Aldehydes **4**–**6** were completely characterized by ^1H NMR, ^{13}C NMR, UV–VIS and FT-IR spectroscopy as well as by mass spectrometry and exhibit very similar properties to ketones **2** and **3**. The *trans* configuration at the C=C double bonds in **6** and **7** was determined by NOE NMR spectroscopy.

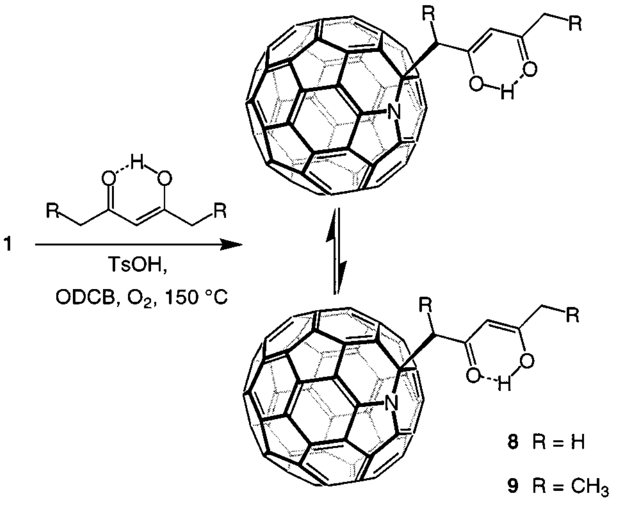
The corresponding reactions of **1** with 1,3-diketones afforded the functionalized azafullerene derivatives **8** and **9** (Scheme 3) which were completely characterized. The fact that the addition proceeded exclusively at the terminal instead of the central C-atoms of the 1,3-diketones is presumably due to steric hindrance. The tautomerization within **8** is comparatively fast on the NMR timescale because only one set of signals for the protons of the addend are found. In the ^1H NMR spectrum of **9**, however, two sets of signals for the two corresponding tautomers are found, indicating a much slower process. This is also demonstrated by the fact that the two individual signals for the protons of the hydrogen bridges at δ 15.91 and 15.82 are much sharper than those of **8**. In the reaction mixture obtained from the treatment of **1** with heptane-3,5-dione, in addition to **9** another component **10**, with a simpler ^1H NMR spectrum showing one set of signals for magnetically equivalent methyl,



Scheme 1

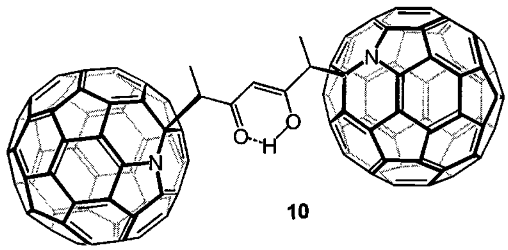


Scheme 2



Scheme 3

methine, enol and olefinic protons, could be detected. The spectroscopic data of **10** are consistent with a bisadduct formed as a side product.



10

The findings of this contribution support the formation of $C_{59}N^+$ from the dimer **1** after thermolysis and oxidation of the radical $C_{59}N$ (Scheme 4). In the arylations reported previously[1] $C_{59}N^+$ serves as electrophile for the attack of electron-rich aromatics. In the present cases it reacts here with enolizable ketones and aldehydes to afford Mannich bases involving a heterofullerene sphere (Scheme 4). This new derivatization method of $C_{59}N$ opens up a facile access to a broad variety of new functionalized heterofullerenes.

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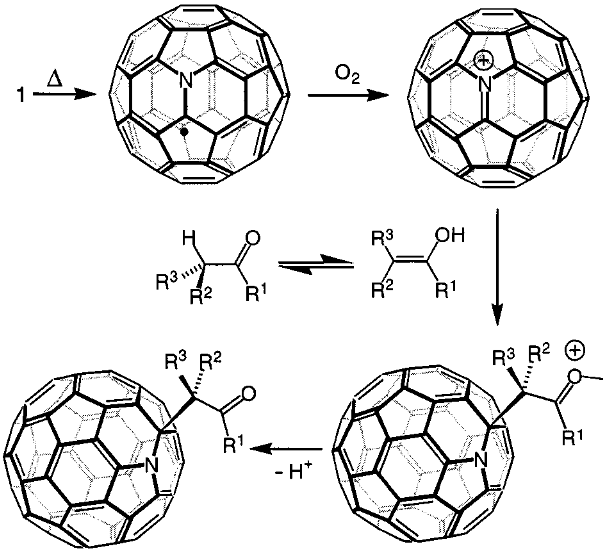

Scheme 4

Notes and references

† *Selected data* for **2**: ν(KBr)/cm^{-1} 2920, 2850, 1729, 1582, 1550, 1509, 1459, 1437, 1422, 1387, 1358, 1317, 1291, 1237, 1185, 1166, 1145, 1118, 1092, 779, 765, 745, 730, 721, 613, 579, 568, 554, 524, 499 and 482; λ_{max}(CH_2Cl_2)/nm 257, 320, 445, 589 and 724; δ_H(400 MHz, CS_2–20% $CDCl_3$) 4.91 (s, 2H) and 2.79 (s, 3H); δ_C(100.5 MHz, CS_2–20% $CDCl_3$) 201.80 (C=O, 1C), 154.94 (2C), 148.31 (2C), 147.37 (2C), 147.11 (2C), 146.90 (4C), 146.38 (2C), 146.31 (2C), 146.02 (2C), 145.75 (2C), 145.50 (2C), 144.90 (2C), 144.74 (2C), 144.14 (4C), 143.79 (2C), 142.89 (2C), 142.54 (2C), 141.88 (2C), 141.56 (2C), 141.22 (2C), 141.01 (2C), 140.83 (2C), 140.78 (2C), 139.43 (2C), 137.41 (2C), 137.35 (2C), 127.26 (2C), 124.63 (2C), 78.37 (1C), 53.84 (CH_2, 1C) and 30.90 (CH_3, 1C); *m/z* (EI) 772 (M^+) and 722 ($C_{59}N^+$). For **3**: ν(KBr)/cm^{-1} 3054, 2950, 2851, 1692, 1594, 1579, 1550, 1446, 1422, 1393, 1344, 1317, 1290, 1215, 1197, 1175, 1092, 1045, 987, 769, 746, 732, 721, 703, 685, 644, 577, 568, 524, 504, 481, 470 and 429; λ_{max}(CH_2Cl_2)/nm 257, 320, 445, 589 and 724; δ_H(400 MHz, CS_2–20% $CDCl_3$) 8.40 (m, 2H), 7.74 (m, 1H), 7.67 (m, 2H) and 5.45 (s, 2H); δ_C(100.5 MHz, CS_2–20% $CDCl_3$) 193.80 (C=O, 1C), 155.02 (2C), 148.57 (2C), 147.57 (1C), 147.36 (2C), 147.10 (2C), 146.93 (2C), 146.87 (2C), 146.34 (2C), 146.26 (2C), 145.97 (2C), 145.73 (2C), 145.55 (1C), 145.44 (2C), 144.85 (2C), 144.71 (2C), 144.09 (4C), 143.77 (2C), 142.85 (2C), 142.54 (2C), 141.83 (2C), 141.53 (2C), 141.18 (2C), 141.03 (2C), 140.80 (2C), 140.75 (2C), 139.39 (2C), 137.42 (2C), 136.58 (2C), 134.93 (i-Ar, 1C), 133.50 (p-Ar, 1C), 128.76 (Ar, 2C), 128.23 (Ar, 1C), 124.78 (2C), 78.59 (1C) and 49.45 (CH_2, 1C); *m/z* (EI) 841 (M^+) and 722 ($C_{59}N^+$). Mannich bases **4**–**6**, **8** and **9** were also completely characterized and exhibit comparable spectroscopic properties. In particular, the UV–VIS spectra of all compounds are virtually identical and the resonances of the C-atoms of the fullerene core in the ^{13}C NMR spectra are very similar.

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