

# 1,3-Dipolar cycloaddition reaction of [60] fullerene and trifluoromethyloxazolones: synthesis of 3-phenyl-5-trifluoromethyl-3,4-dihydropyrrolo[60] fullerene

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## Abstract

1,3-Dipolar cycloaddition of trifluoromethyloxazolone to C<sub>60</sub> affords 3-phenyl-5-trifluoromethyl-3,4-dihydropyrrolo[60] fullerene. The novel compound was characterized by <sup>13</sup>C and <sup>1</sup>H NMR as well as FD-MS, FT-IR and UV-Vis spectroscopies. © 1998 Elsevier Science S.A. All rights reserved.

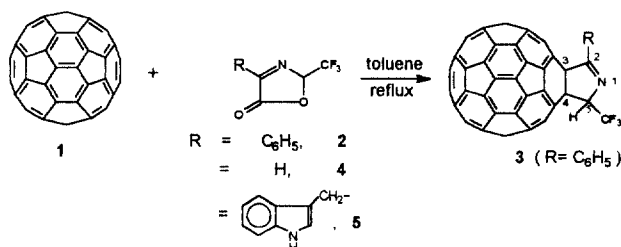
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The functionalization of [60] fullerene has been an area of growing interest during the past few years [1,2]. Among the large number of functionalization reactions of C<sub>60</sub>, the 1,3-dipolar cycloaddition reaction is one of the most powerful and versatile methods for derivatising fullerenes [3–5]. Since organofluorine compounds have unique physical and chemical properties, it is very interesting to synthesize and study fluorine-containing C<sub>60</sub> derivatives. Tian et al. [6] recently reported an efficient way for the synthesis of trifluoromethylpyrroles and related compounds from easily prepared trifluoromethyloxazolones via 1,3-dipolar cycloaddition. Here, we wish to report the synthesis of trifluoromethyl substituted C<sub>60</sub> derivatives by 1,3-dipolar cycloaddition reaction between C<sub>60</sub> and trifluoromethyloxazolones.

In a typical procedure for the cycloaddition, C<sub>60</sub> (73 mg) and trifluoromethyl-oxazolone **2** (135 mg) were dissolved in toluene (100 ml). During refluxing, the solution changed the colour from purple to dark brown. After 6–7 days, TLC indicated a new compound. The solvent was then removed by rotary evaporation under vacuum. Isolation by flash column chromatography on silica gel using *n*-hexane, toluene and methylene chloride as eluents afforded 10.9 mg **3** in 66% yield (based on consumed C<sub>60</sub>).

An adduct could be detected by TLC when oxazolone **4** was used as the substrate, while no adduct was formed in the case of sterically hindered oxazolone **5** under similar reaction conditions. Compared with the reaction of ordinary oxazolones that only took 24 h [7], the reaction of trifluoromethyl-oxazolones with C<sub>60</sub> was much slower, which reflects the lower consequent electron density of the addend. A more rapid reaction is found by electron availability in the addend.

The structure of the fullerene derivative **3** was characterized spectroscopically. The field desorption mass spectrum (FD-MS) of **3**, which showed the molecule ion peak at *m/z* 905 (C<sub>60</sub>H<sub>6</sub>F<sub>3</sub>N) as base peak together with another peak at *m/z* 720 due to the C<sub>60</sub> fragment agree with the proposed structure **3**. <sup>1</sup>H NMR (600 MHz, CS<sub>2</sub>/d<sub>6</sub>-acetone) shows doublets for two aromatic protons at 8.1 ppm with *J* = 6.3 Hz, complex multiplets for three aromatic protons at 7.56–7.60 ppm and one quartet for the C5-H at 6.75 ppm with <sup>3</sup>J<sub>H-F</sub> = 7.3 Hz. <sup>19</sup>F NMR (282.4 MHz, CS<sub>2</sub>/d<sub>6</sub>-acetone) showed one singlet for the CF<sub>3</sub> group at 14.4 ppm. In accor-



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dance with  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR,  $^{13}\text{C}$  NMR spectra (150.9 MHz,  $\text{CS}_2/\text{d}_6\text{-acetone}$  with  $\text{Cr}(\text{acac})_3$  as relaxation reagent), showed  $\text{CF}_3$  carbon at 125.36 ppm, aryl carbons at 129.23(2C), 129.84(2C), 131.57(1C) and 134.93(1C) ppm. The  $\text{C}=\text{N}$  carbon appeared at 175.19 ppm. Since the structure of adduct **3** has  $\text{C}_1$  symmetry, there should be sixty signals for the  $\text{C}_{60}$  skeleton. In the spectrum, there were 45 signals for the cage, some of which were overlapped. The signals for added site  $\text{sp}^3$  carbons, i.e., C3 and C4, were at 85.93 and 72.29 ppm respectively. It is reasonable to assume that in the molecule of the product, C2 and C5 were linked on a 6–6 junction of the fullerene cage as shown in the figure.

Some of spectra data of **3**.

$^{13}\text{C}$  NMR (150.9 MHz,  $\text{CS}_2/\text{d}_6\text{-acetone}$  with  $\text{Cr}(\text{acac})_3$  as relaxation reagent): 72.29(1C,  $\text{sp}^3$  carbon for  $\text{C}_{60}$ ), 85.64(1C,  $\text{C}-\text{CF}_3$ ), 85.93(1C,  $\text{sp}^3$  carbon for  $\text{C}_{60}$ ), 125.36( $\text{CF}_3$ ), 129.23(2C, aryl), 129.84(2C, aryl), 131.57(1C, aryl), 134.22(1C), 134.93(1C, aryl), 136.37(1C), 136.48(1C), 136.92(1C), 140.08(1C), 140.63(1C), 140.66(1C), 140.85(1C), 142.22(1C), 142.28(3C), 142.45(2C), 142.69(1C), 142.71(2C), 142.91(1C), 142.99(1C), 143.23(1C), 143.30(2C), 143.41(1C), 143.66(1C), 143.71(1C), 144.50(1C), 144.65(1C), 144.86(2C), 145.04(1C), 145.66(1C), 145.86(1C), 145.92(4C), 146.01(1C), 146.15(1C), 146.22(1C), 146.45(1C), 146.52(3C), 146.66(2C), 146.76(1C), 146.92(1C), 146.96(1C), 147.09(1C), 147.12(1C), 147.52(1C), 147.57(1C), 147.91(2C), 149.83(2C), 153.64(2C), 175.19( $\text{C}=\text{N}$ ) ppm.

The assignment of  $^{13}\text{C}$  NMR peak at 72.29 and 85.93 to C4 and C3 carbons was based on our unreported results of the similar compound without the trifluoromethyl group.

Because the peak at 85.64 was a quartet and had a higher intensity, we assign this peak to the C5 carbon attached to a proton.

IR(KBr): 2959.4, 2926.6, 2852.7, 1718.7, 1646.9, 1509.4, 1459.4, 1359.4, 1175.0, 1150.0, 1100.0, 1050.0, 1031.1, 868.8, 803.1, 762.5, 693.8, 575.0, 528.1  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CS}_2/\text{d}_6\text{-acetone}$ ): 8.10 (2H, d,  $J=6.3$  Hz, aryl-H), 7.60–7.56(3H, m, aryl H), 6.75 (1H, q,  $^3J_{\text{H-F}}=7.3$  Hz,  $\text{H}-\text{C}-\text{CF}_3$ ) ppm.  $^{19}\text{F}$  NMR (282.4 MHz,  $\text{CS}_2/\text{d}_6\text{-acetone}$ ): 14.4 ppm. FD-MS:  $m/z$  905 ( $\text{M}^+$ , 100), 720( $\text{C}_{60}$ ). UV-Vis ( $n$ -hexane): 245, 300, 335, 365 nm.

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