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An Unexpected Reaction: [2 + 1] Cycloaddition of [60]Fullerene with 4, 4, 5, 5-Tetramethylimidazolidine-2-Thione and DL-Valine

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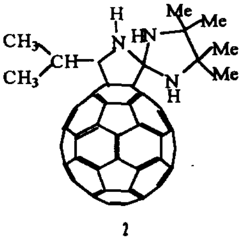
Abstract: C_{60} reacted with DL-valine and 4, 4, 5, 5-tetramethylimidazolidine-2-thione in a new reaction to give a new C_{60} spiro-compound **3** which was characterized by FT-IR, NMR, and FD-mass spectra. The possible reaction mechanism was put forward .

The fascinating structures and properties of fullerenes have opened a new field of chemistry. In the past studies in this area, both experimental and theoretical results indicated the electron-deficient character of fullerenes [1], such as nucleophilic addition [2], radical addition [3], cycloaddition including [4 + 2] cycloaddition [4], [3 + 2] 1,3 - dipolar cycloaddition [5], [2 + 2] cycloaddition [6], [1 + 2] cycloaddition [7] et al. In the methods for [60]fullerene functionalization, the [3 + 2] 1,3- dipolar cycloaddition was of special significance. Recently, we have studied some 1,3- dipolar cycloaddition reactions of C_{60} and azomethine ylide which can be generated in situ from the reaction of α -aminoacid with aldehyde or ketone[8] to yield pyrrolidino[60]fullerene. We also tried to establish a new synthesis route that [60]fullerene reacted with azomethine ylide generated from thione **1** and α - aminoacid through 1,3- dipolar cycloaddition to form a novel closed [6, 6] pyrrolidino[60]fullerene (compound **2**) which can be oxidized to a stable binitroxide possibly possessing special physical properties. However, the result of experiment showed that the product was not our expected compound **2**. According to the results of characterization , it was compound **3** (Scheme 1). Here we report the interesting results of the experiment and characterization.



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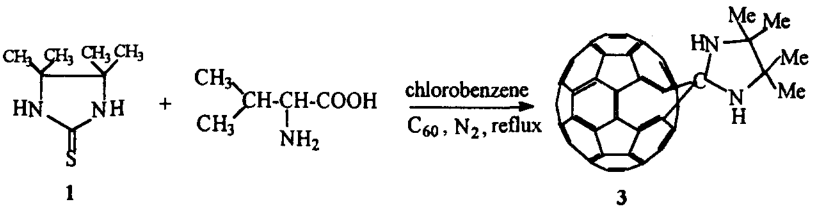


Scheme 1

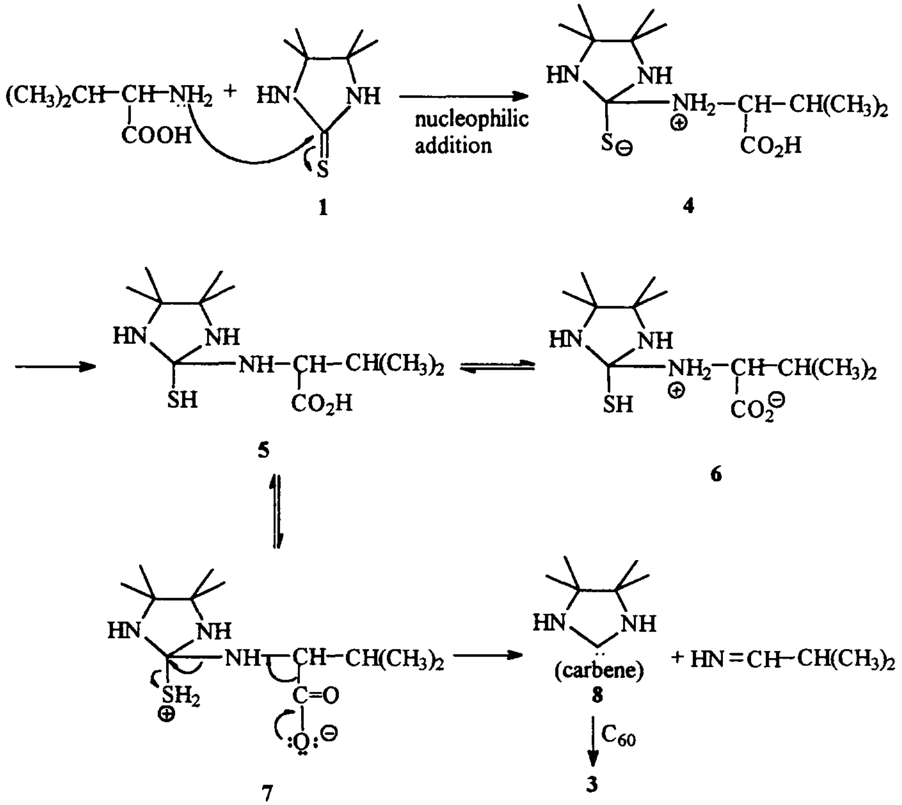
A mixture of C_{60}, DL-valine and 4, 4, 5, 5-tetramethylimidazolidine-2-thione **1** [9] (1 : 2: 5 molar equiv) in dry chlorobenzene was stirred and refluxed under nitrogen for 20 h. After being quenched, the reaction mixture was concentrated in vacuo. The compound **3** was isolated by common column chromatography on silica gel using a mixture of petroleum ether and toluene (v/v 1 : 3, $R_f = 0.50$) as eluent, yield 34.9 %, (based on converted C_{60}).

The FD-mass spectrum shows a peak at 847 (relative intensity, 100 %, M^+ for $C_{67}H_{14}N_2$) with the peak for [60]fullerene at 721 (relative intensity 82 %) which loses the fragment of $C_7H_{14}N_2$. In the FT-IR spectrum (KBr pellet) [10], there are four bands at 1428.0 , 1183.5, 574.3 and 527.4 cm^{-1} corresponding to vibration of [60]fullerene skeleton, and the 3271.2 cm^{-1} suggests the presence of N- H bond.

The NMR spectra [11] give more information of structural feature of compound **3**. The ^{13}C-NMR spectrum exhibits 33 signals, of which 27 signals correspond to the [60]fullerene framework [4 x 1 C, 20 x 2 C, 1 x 4 C, 2 x 6 C]. The chemical shift of two tertiary-carbons of imidazolidine is at δ 78.94, and the spiro- carbon atom is located at δ 79.70. The resonance of two sp^3 hybridized carbon atoms in a closed [6, 6] fullerene derivative is not observed; however, we note that the ^{13}C-NMR spectrum exhibits exactly the required number of lines (with the correct intensities), the structure of the compound **3** is proved to be an open [5, 6] adduct [12]. The other three signals with one signal unresolved are carbon atoms of four methyl groups, this reveals that the four methyl groups of imidazolidine are not equivalent, which is also demonstrated by the ^1H- NMR spectrum.

The possible mechanism of the reaction of C_{60} with compound **1** and α - aminoacid to give compound **3** is outlined as following (Scheme 2): the nucleophilic amino group of α - aminoacid first attacks the carbon atom of thiocarbonyl group to form **4**. The acid-base reaction or acid-base equilibrium occurs among **4** ~ 7. **6** or 7 first loses CO_2 and H_2S then breaks one of the C-N bonds to form carbene **8**, finally **8** and C_{60} undergo [1 + 2] cycloaddition to afford **3**. In our experiment, we find that the reaction does not occur when C_{60} reacts with compound **1** in the absence of α - aminoacid.

In summary, we have synthesized a new C_{60} derivative by a novel way, and its structure has been confirmed by ^1H-NMR, ^{13}C-NMR, FT-IR and MS spectra. The investigating of the reactions is under progress in detail.



Scheme 2

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10. FT-IR spectrum of compound **3** (KBr, pellet) 3271.2, 2953.9, 2923.12, 1462.7, 1428.0, 1390.4, 1183.5, 1023.4, 864.0, 824.5, 781.8, 574.3, 527.4 cm^{-1}.
11. The NMR spectra of the compound **3**: ^{13}C-NMR (125 MHz, $CS_2/CDCl_3$) δ 128.11 (2 C), 128.63 (2 C), 135.25 (2 C), 136.31 (2 C), 139.49 (2 C), 139.56 (2 C), 141.51 (2 C), 141.70 (2 C), 141.99 (2 C), 142.11 (2 C), 142.44 (2 C), 142.56 (4 C), 142.90 (1 C), 143.20 (1 C), 144.12 (2 C), 144.38 (2 C), 145.01 (6 C), 145.12 (2 C), 145.36 (1 C), 145.57 (1 C), 146.76 (6 C), 146.00 (2 C), 146.08 (2 C), 146.55 (2 C), 146.75 (2 C), 153.52 (2 C), 155.08 (2 C), 78.94 (2 C, two tertiary-carbons of imidazolidine), 79.70 (1 C , spiro- carbon), 29.83 (1 C), 29.62 (1 C), 23.74 (1 C), 19.53 (1 C). The ^1H- NMR spectrum (500 MHz, $CS_2/CDCl_3$) δ 2.94 (s, br, 2 H), 1.43 (m, J = 6 Hz, 6 H, 2 CH_3), 1.56 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3).
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