Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 48 (2007) 4635–4638

Tetrahedron Letters

Revisit to the reaction of [60]fullerene with nitrile ylides generated from imidoyl chlorides and triethylamine

Guan-Wu Wang* and Hai-Tao Yang

Hefei National Laboratory for Physical Sciences at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

Received 10 January 2007; revised 16 April 2007; accepted 16 April 2007
Available online 22 April 2007

Abstract—The reaction of [60]fullerene (C_{60}) with nitrile ylides generated from *N*-benzyl-4-nitrobenzimidoyl chloride/*N*-(4-chlorobenzyl)-4-nitrobenzimidoyl chloride and triethylamine gave only isomeric monoadducts of C_{60} with [6,6]-closed structure. No [5,6]-open adduct of C_{60} could be identified from these reactions. The previously reported [5,6]-open product of C_{60} should be reassigned as a [6,6]-closed product.

A variety of methods have been developed to functionalize fullerenes.[1] Among these methods, cycloaddition reactions, especially 1,3-dipolar cycloaddition reactions, have been widely employed to synthesize fullerene derivatives. Usually, a cycloaddition reaction occurs at a [6,6]-double bond rather than a [5,6]-single bond of [60]fullerene (C_{60}). The common product types of C_{60} are [6,6]-closed adducts and [5,6]-open adducts. [5,6]-Open adducts such as fulleroids and azafulleroids are normally secondary products and are produced by extrusion of N_2 from the initially formed C_{60}-fused pyrazolines and triazolines.[1]

Misassignments of fullerene products were occasionally encountered in the literature. For example, the reported [5,6]-closed adducts generated from the thermal reaction of C_{60} with azidoformates[2] were later proved to be [5,6]-open adducts by Hirsch's group[3] and Smith's group.[4] The 1,3-dipolar reaction of C_{60} with the nitrile ylide generated from *N*-benzyl-4-nitrobenzimidoyl chloride and triethylamine (Et_3N) has been investigated independently by two research groups.[5,6] Wu et al.[5] isolated two isomeric C_{60}-fused pyrroline derivatives along with a minor C_{60}-fused pyrrolidine derivative. The latter was resulted from the direct reaction of C_{60} with Et_3N. All of these products were [6,6]-closed adducts. However, Ovcharenko et al.[6] later claimed that they obtained a C_{60}-fused pyrroline derivative and two diastereomeric [5,6]-open isomers. The only obvious variation between the two reaction conditions is the different temperatures: Wu et al. conducted the reaction at room temperature while Ovcharenko et al. ran the reaction at 130 °C. Surprised by the different products that were claimed from the same reaction[5,6] and the two [5,6]-open isomers from the direct 1,3-dipolar cycloaddition reaction of C_{60},[6] we decided to reinvestigate the reaction in order to clarify the inconsistence in the literature. In this Letter, we report our results regarding this issue.

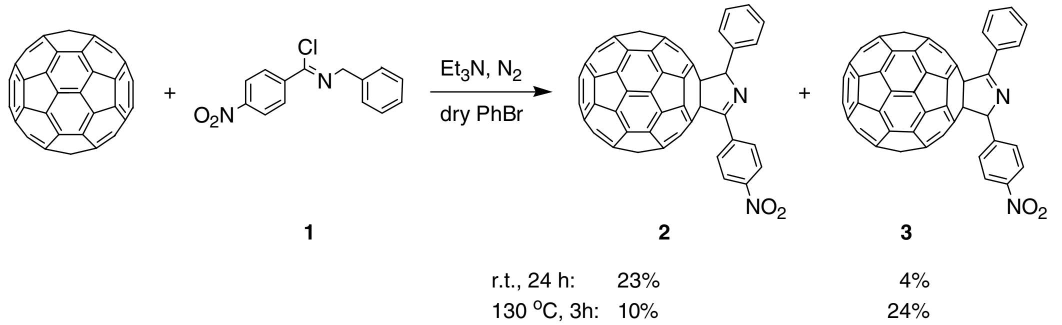
Previously, a large excess of Et_3N was used in the procedure by Wu et al.[5] To compare the result at room temperature with that at 130 °C, we examined the reaction of C_{60} (50.0 mg) with *N*-benzyl-4-nitrobenzimidoyl chloride (**1**, 30.0 mg) and Et_3N (12.5 mg) (the same molar ratio of 1:1.5:1.75 as that by Ovcharenko et al.) at room temperature in dry bromobenzene (17 mL) under atmosphere of nitrogen. After stirring for 24 h at room temperature, the reaction mixture was evaporated to dryness in vacuo. The residue was separated on a silica gel column with CS_2–toluene as the eluent to afford unreacted C_{60} (30.1 mg, 60%) and then the same isomeric [6,6]-closed adducts **2** (15.4 mg, 23%) and **3** (2.6 mg, 4%)[7] (Scheme 1) as those in the previous report.[5] It should be noted that the fullerene products were washed with diethyl ether to remove any organic contaminants before weighting and spectral measurements. The C_{60}-fused pyrrolidine derivative

---

Keywords: [60]Fullerene; Nitrile ylide; Imidoyl chloride; 1,3-Dipolar reaction; Cycloaddition.

* Corresponding author. Tel./fax: +86 551 360 7864; e-mail: gwang@ustc.edu.cn

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.04.085



Scheme 1.

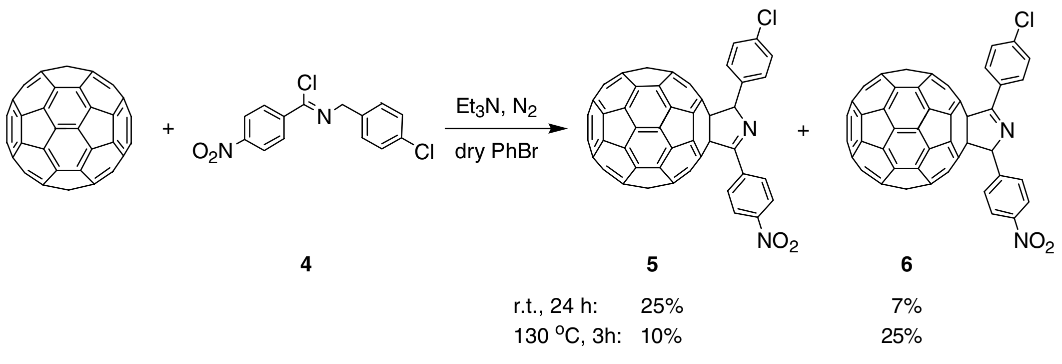
formed from the direct reaction of C_{60} and Et_3N was not isolated, probably because much less amount of Et_3N was utilized under the present reaction conditions.

Then, the reaction of C_{60} with imidoyl chloride **1** and Et_3N in a molar ratio of 1:1.5:1.75 at 130 °C in dry bromobenzene under atmosphere of nitrogen for 3 h was repeated according to the described procedure by Ovcharenko et al.[6] A purple band for unreacted C_{60} and two brown bands by column chromatography on silica gel were collected and characterized. The first brown band corresponded to fulleropyrroline **2**, just as previously reported.[6] However, the product in the second brown band was the same as that for the room-temperature reaction, and was proved to be fulleropyrroline **3** by comparison of its TLC, HPLC and NMR data with those of authentic sample of compound **3**. The isolated yields for products **2** and **3** were 10% and 24%, respectively, along with 50% of recovered C_{60}. No other isomeric monoadduct of C_{60} except for products **2** and **3** could be obtained. In sharp contrast with that reported by Ovcharenko et al.,[6] there was no evidence showing the existence of [5,6]-open isomer.

We suspected that only one signal in the sp^3-carbon region at 87.74 ppm was observed by Ovcharenko et al.,[6] probably due to the poor signal/noise ratio of their ^{13}C NMR spectrum, thus leading to the wrong assignment of product **3**. The assumed another isomeric monoadduct with a [5,6]-open structure was probably misled by the ^1H NMR spectrum of their sample containing some contaminant. To confirm our assumption, we collected all fractions besides the first purple band for C_{60} and the two brown bands for fullerene products. All fractions were evaporated to dryness and subject to ^1H NMR measurements without washing the samples. It was found that the brown band for product **2** was contaminated by 4-nitrobenzonitrile and 4-nitrobenzaldehyde, and the fractions before the first and second brown bands contained 4-nitrobenzonitrile and 4-nitrobenzaldehyde, respectively. The brown band for product **3** was contaminated by 4-nitrobenzaldehyde. In a control experiment, it was found that 4-nitrobenzonitrile and 4-nitrobenzaldehyde were indeed formed by treating imidoyl chloride **1** with Et_3N at 130 °C in dry bromobenzene under atmosphere of nitrogen. These impurities could be washed away from the samples of fulleropyrrolines **2** and **3** by diethyl ether.

In order to further substantiate that [5,6]-open adducts could not be produced from the direct 1,3-dipolar cycloaddition reaction of C_{60} with nitrile ylides, we investigated the reaction of C_{60} (50.0 mg) with *N*-(4-chlorobenzyl)-4-nitrobenzimidoyl chloride (**4**, 32.5 mg) and Et_3N (12.5 mg) at room temperature and 130 °C in dry bromobenzene (17 mL) under atmosphere of nitrogen according to the above procedures for the reaction of C_{60} with imidoyl chloride **1** and Et_3N, respectively. Two isomeric [6,6]-closed adducts **5** and **6** were obtained in the yields of 25% and 7% along with 54% of recovered C_{60} at room temperature, while 10% and 25% together with 40% of recovered C_{60} at 130 °C (Scheme 2).

Fulleropyrrolines **5** and **6** were fully characterized by MS, ^1H NMR, ^{13}C NMR, IR and UV–vis spectra.[8] The UV–



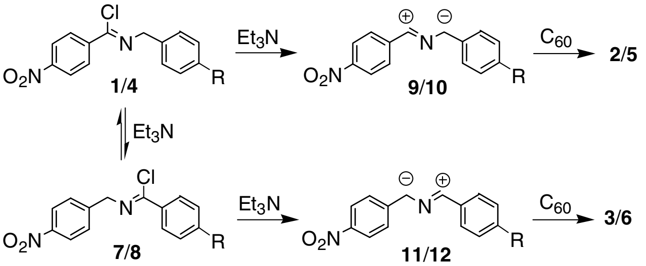
Scheme 2.

vis spectra of adducts **5** and **6** clearly gave an absorption at 428 nm, which is typical for a 1,2-adduct with [6,6]-closed structure. In the ^{1}H NMR of adducts **5** and **6**, the methine proton in adduct **6** was more downfield shifted relative to that in adduct **5** due to the stronger electron-withdrawing property of the nitro group, the same phenomenon was observed in the corresponding counterparts **3** and **2**.[5] The ^{13}C NMR spectra of products **5** and **6** (Fig. 1) displayed similar patterns for the two isomers, and more importantly, exhibited two sp^3-carbons of the C_{60} skeleton at 84.12 and 77.33 ppm and one methine carbon at 87.59 ppm for fulleropyrroline **5**, while at 84.32, 77.00 and 87.04 ppm for fulleropyrroline **6**, respectively.

The above results demonstrated that only [6,6]-closed adducts were produced from the reaction of C_{60} with nitrile ylides generated from imidoyl chlorides and Et_3N, consistent with the previous reports on the 1,3-dipolar reaction of C_{60} with nitrile ylides formed by other routes.[9]

Interestingly, it was observed that the product distributions of adduct **2** versus adduct **3** and adduct **5** versus adduct **6** were reversed in favor of the formation of adducts **3** and **6** when the reaction temperature was raised from room temperature to 130 °C. It was believed that the higher temperature facilitated the tautomerization of imidoyl chlorides **1** and **4** to imidoyl chlorides **7** and **8**, which would give more favorable 1,3-dipoles **11** and **12**. The cycloaddition of dipoles **11** and **12** to C_{60} should afford more adducts **3** and **6** (Scheme 3).

In summary, the reaction of C_{60} with nitrile ylides generated from imidoyl chlorides and Et_3N gave only isomeric monoadducts with [6,6]-closed structure. No



1, **7**, **9**, **11**: R = H; **4**, **8**, **10**, **12**: R = Cl

Scheme 3.

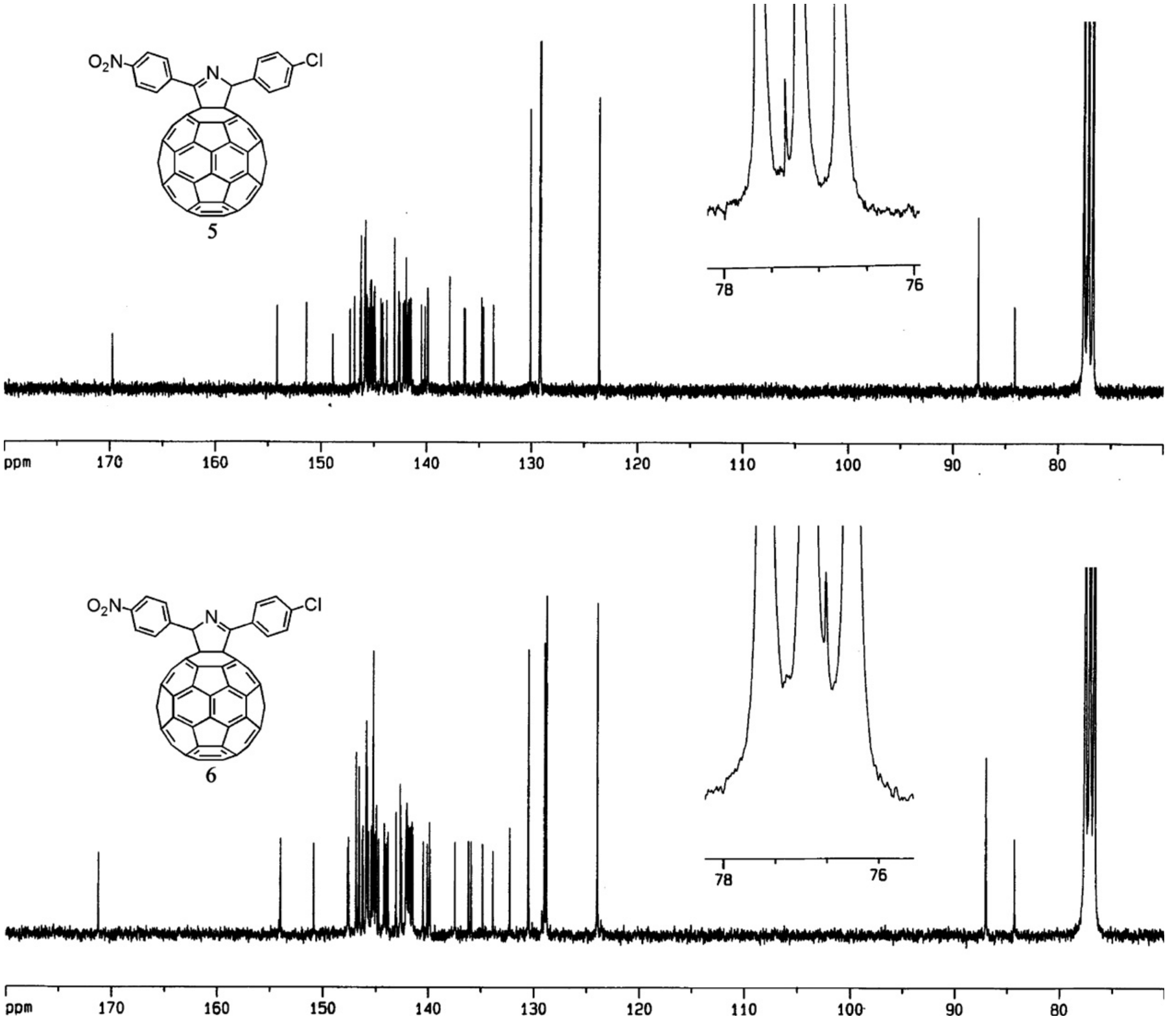


Figure 1. ^{13}C NMR spectra of fulleropyrrolines **5** and **6**.

[5,6]-open adduct of C_{60} could be isolated from the reaction mixtures. The previously reported [5,6]-open product was misassigned and should be corrected as the [6,6]-closed product.

Acknowledgement

The authors are grateful for the financial support from the National Natural Science Foundation of China (Nos. 20572105 and 20621061).

References and notes

1. For reviews, see: (a) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685; (b) Hirsch, A. *Synthesis* **1995**, 895; (c) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
2. Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Smith, P. R. R.; Millar, J. R. A.; Parkinson, J. A.; Rankin, D. W. H.; Taylor, A. T. *J. Chem. Soc., Chem. Commun.* **1995**, 887.
3. Schick, G.; Grösser, T.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2289.
4. Smith, A. B.; Tokuyama, H. *Tetrahedron* **1996**, *52*, 5257.
5. Wu, S.-H.; Wang, G.-W.; Shu, L.-H.; Wu, H.-M.; Jiang, S.-K.; Xu, J.-F. *Synth. Commun.* **1997**, *27*, 1415.
6. Ovcharenko, A. A.; Chertkov, V. A.; Karchava, A. V.; Yurovskaya, M. A. *Tetrahedron* **1997**, *38*, 6933.
7. The yields of **2**, **3** and the C_{60}-fused pyrrolidine derivative in Ref. 5 were misplaced and should be 43%, 8% and 2%, respectively, based on consumed C_{60}.
8. *Spectral data for* **5**: ^{1}H NMR (300 MHz, CS_2–$CDCl_3$) δ 8.44 (d, $J = 8.9$ Hz, 2H), 8.37 (d, $J = 8.9$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.18 (s, 1H); ^{13}C NMR (75.5 MHz, CS_2–$CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 169.74 (N=*C*), 154.17, 151.41, 148.91, 147.28, 146.88, 146.85, 146.33, 146.28, 146.24 (2C), 145.87 (2C), 145.85, 145.81 (2C), 145.70, 145.66, 145.48, 145.34, 145.32, 145.29, 145.26, 145.24, 145.09, 145.00, 144.96, 144.94, 144.90, 144.36, 144.25, 144.18, 143.80, 143.77, 143.07 (2C), 142.68, 142.65, 142.60, 142.54, 142.21, 142.13, 142.08, 141.95, 141.94 (2C), 141.90, 141.74, 141.66, 141.60, 141.51, 141.47, 140.48, 140.15, 139.93, 139.91, 139.85, 137.83, 136.41, 136.34, 134.76, 134.62, 133.65, 130.13 (2C, aryl C), 129.24 (2C, aryl C), 129.16 (2C, aryl C), 123.61 (2C, aryl C), 87.59 (Ar*C*H), 84.12 (sp^{3}-*C* of C_{60}), 77.33 (sp^{3}-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2971, 2922, 2852, 1597, 1521, 1490, 1429, 1410, 1344, 1269, 1183, 1092, 1043, 1015, 986, 858, 847, 825, 750, 692, 612, 574, 527; MS (+APCI) 992. *Spectral data for* **6**: ^{1}H NMR (300 MHz, CS_2–$CDCl_3$) δ 8.33 (d, $J = 8.7$ Hz, 2H), 8.23 (d, $J = 8.5$ Hz, 2H), 7.91 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.25 (s, 1H); ^{13}C NMR (75.5 MHz, CS_2–$CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 171.24 (N=*C*), 154.01, 150.87, 147.67, 147.58, 146.87 (2C), 146.60 (2C), 146.54, 146.25, 146.21, 145.92, 145.90 (3C), 145.81 (2C), 145.70, 145.43, 145.39, 145.28, 145.24 (3C), 145.14, 145.03, 144.95, 144.93, 144.72, 144.22, 144.19, 144.06, 143.87, 143.82, 143.08, 143.06, 142.65 (2C), 142.63, 142.56, 142.14, 142.08, 142.05, 142.03, 142.00, 141.91, 141.81, 141.76, 141.72, 141.57, 141.53, 141.49, 140.49, 140.09, 139.87, 139.85, 137.46, 136.17, 135.92, 134.83, 133.87, 132.29, 130.51 (2C, aryl *C*), 128.99 (2C, aryl *C*), 128.81 (2C, aryl *C*), 124.00 (2C, aryl *C*), 87.04 (Ar*C*H), 84.32 (sp^{3}-*C* of C_{60}), 77.00 (sp^{3}-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2969, 2923, 2853, 1597, 1521, 1489, 1428, 1345, 1275, 1181, 1108, 1093, 1044, 1013, 985, 856, 837, 827, 746, 721, 701, 612, 574, 527; MS (+APCI) 992.
9. (a) Averdung, J.; Albrecht, E.; Lauterwein, J.; Luftmann, H.; Mattay, J.; Hohn, H.; Müller, W. H.; ter Meer, H.-U. *Chem. Ber.* **1994**, *127*, 787; (b) Averdung, J.; Mattay, J. *Tetrahedron* **1996**, *52*, 5407; (c) Reinov, M. V.; Yurovskaya, M. A.; Streletskiy, A. V.; Boltalina, O. V. *Chem. Heterocycl. Compd.* **2004**, *40*, 1150.