Tetrahedron Letters 55 (2014) 3747–3749

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Reactions of fullerene C_{60} with organometallic azides

Arslan R. Akhmetov *, Ildar R. Yarullin, Airat R. Tuktarov, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa 450075, Russia

ARTICLE INFO

Article history:
Received 28 January 2014
Revised 11 March 2014
Accepted 15 May 2014
Available online 23 May 2014

Keywords:
Fullerene C_{60}
Diethylaluminium azide
Tributyltin azide
1,2-Addition
1-Azido-2-alkylfullerene

ABSTRACT

Reactions of fullerene C_{60} with organometallic azides [Et_2AlN_3, $EtAl(N_3)_2$ and Bu_3SnN_3] led to novel 1-azido-2-alkylfullerenes. The structures of the products were confirmed by IR, ^1H and ^{13}C NMR spectroscopy and MALDI TOF mass spectrometry.

Interest in the reactions of fullerenes with organic azides is related to the possibility to obtain functionally substituted compounds which might be useful for medicine and technology.[1,2] The reactions of fullerene C_{60} with organic azides, resulting in the formation of [2+3]-cycloadducts—triazolinofullerenes,[3] or [2+1]-cycloadducts—5,6- and 6,6-azahomofullerenes or 5,6- and 6,6-aziridinofullerenes,[4] are covered extensively in the literature.

We previously demonstrated[5] that the reaction of fullerene C_{60} with hydrazoic acid (HN_3) gave unsubstituted aziridino- or triazolinofullerenes, depending on the reaction conditions, while the reactions of C_{60} with halogen azides (IN_3, BrN_3) led to the formation of novel 1-halo-2-azidofullerenes.[6]

At the beginning of our study, no reports were available on the reactions of fullerene C_{60} with organometallic azides, which, in our opinion, could produce more stable fullerene azide derivatives.

As a further development of the above-mentioned work, and to elaborate an efficient method for the synthesis of previously unknown azidofullerenes, we have performed the first study of the reactions of C_{60} with organometallic azides including Et_2AlN_3, $EtAl(N_3)_2$ and Bu_3SnN_3, which were synthesized via reported procedures.[7,8]

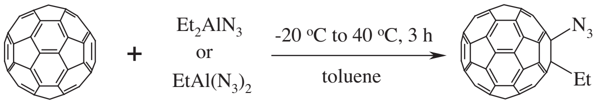
As a model system, we chose the reaction of Et_2AlN_3 with fullerene C_{60} and used it to study the effects of the reaction conditions and reactant ratio on the yield and composition of the reaction products.

It was found that C_{60} fullerene reacted with a fivefold excess of freshly prepared diethylaluminium azide[7] under the developed conditions[9] (−20 °C, followed by heating to 40 °C over 3 h, in toluene as the solvent) to give 1-azido-2-ethyl(C_{60}-I_h)[5,6]fullerene (**1**) in ~20% yield (Scheme 1). Similar results were obtained when Et_2AlN_3 was replaced by $EtAl(N_3)_2$. No reaction took place, with aluminium triazide [$Al(N_3)_3$].

An increase in the time for the reaction between C_{60} and Et_2AlN_3 from three to 24 hours had no effect on the yield or composition of the target azide, and replacement of toluene with chlorobenzene or dichlorobenzene as the solvent resulted in polyadducts.

Compound **1**[10] was isolated by preparative HPLC and characterized by standard analytical methods (IR, ^1H and ^{13}C NMR spectroscopy and MALDI TOF mass spectrometry).

The IR spectrum of adduct **1** exhibited strong absorption bands at 2092, 1632, 1110, 754, 552 and 526 cm^{-1}, which belong to —N=N— bond vibrations characteristic of N_3 and the fullerene core. The MALDI TOF mass spectrum showed only one ion at *m*/*z* 749.040, due to the $[C_{60}C_2H_5]^-$ fragment. Unfortunately, we did not observe a molecular ion corresponding to the formula $C_{62}H_5N_3$. Apparently, MALDI ionization of molecule **1** using a UV laser induces elimination of the azide group, and thus we only observe the corresponding $[M-N_3]^-$ ion.



1

Scheme 1.

---

* Corresponding author. Tel./fax: +7 3472842750.
E-mail address: TuktarovAR@gmail.com (A.R. Akhmetov).

http://dx.doi.org/10.1016/j.tetlet.2014.05.070
0040-4039/© 2014 Elsevier Ltd. All rights reserved.

The ^{13}C NMR spectrum of compound **1** exhibited 29 signals due to the sp^2-hybridized carbon atoms of the fullerene cage at 134–155 ppm, and two signals for the sp^3-hybridized carbon atoms of C_{60} linked to the azide and ethyl groups (79.91 and 65.93 ppm, respectively). In the HMBC experiment on monoadduct **1**, cross peaks were observed between the methylene hydrogen atom of the ethyl group and the carbon atoms in the α- and β-environment (Fig. 1).

To prove more reliably the structure of 1-azido-2-ethyl (C_{60}-I_h)[5,6]fullerene (**1**), namely the presence of the azido group in these molecule, we have further transformed the azido group. Thus, the reaction of azidofullerene **1** with PPh_3 in dry toluene at room temperature led to the formation of phosphine imide **2** in quantitative yield (Scheme 2).[11]

The MALDI TOF mass spectrum exhibited a molecular ion peak at m/z 1025.208 (for $C_{80}H_{20}NP$, ca. m/z 1025.995) and a fragment ion peak at m/z 996.137 due to $[M-Et]^+$. In the IR spectrum of the adduct **2**,[12] no absorption band at ca. 2092 cm^{-1} characteristic of the azido group was present. The ^{13}C NMR spectrum displayed 29 signals due to the sp^2 hybridized carbon atoms of the fullerene cage, while the sp^3 hybridized carbon atoms of C_{60} were responsible for the signals at 79.89 and 65.93 ppm, being due to the carbon atoms bearing the phosphine imide and the ethyl groups, respectively. The presence of a phosphorus atom between the nitrogen atom and the phenyl substituents caused doublet splitting signals for the α, β and γ carbon atoms of the phenyl substituents in the ^{13}C NMR spectrum with the corresponding constants $^1J_{P-C}$, $^2J_{P-C}$ and $^3J_{P-C}$. The maximum value of the spin–spin coupling constant (SSCC) for a fixed α carbon atom at the phosphorus atom was $^1J_{P-C} = 45.28$ Hz, while the SSCCs of the β and γ carbon atoms of the phenyl substituent were $^2J_{P-C} = 12.07$ Hz and $^3J_{P-C} = 10.06$ Hz, respectively.

In order to extend the scope of this method, we have developed the synthesis of alkylazidofullerenes, via the reaction of C_{60} with Sn-containing azides. In analogy with Et_2AlN_3 and $EtAl(N_3)_2$, Bu_3SnN_3 reacted with C_{60} fullerene under the developed conditions[13] (100 °C, 1 h, chlorobenzene as the solvent) only in the presence of a stoichiometric amount of $Cu(OTf)_2$ to give 1-azido-2-butyl(C_{60}-I_h)[5,6]fullerene (**3**) in a yield of ~30% (Scheme 3). In the absence of $Cu(OTf)_2$, the reaction did not occur. The use of $Cu(OTf)_2$ in an equimolar amount with respect to C_{60} was optimal; therefore, even a slight decrease in its quantity (for example, to 70–80 mol %) decreased sharply the yield of the target adduct **3**. An increase in the concentration of $Cu(OTf)_2$ did not improve the yield of **3** further.

As in the case of **1**, the structure of compound **3**[14] was reliably determined by standard analytical methods (IR, ^1H and ^{13}C NMR spectroscopy and MALDI TOF MS).

An increase in the time for the reaction between C_{60} and Bu_3SnN_3 from one to three hours led to the formation of polyadducts, which were difficult to separate or identify. Replacement of chlorobenzene by toluene, or a decrease in the reaction temperature to 40 °C resulted in yields of compound **3** not exceeding 5%.

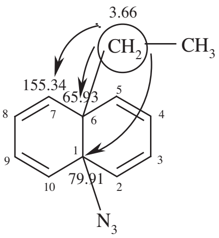
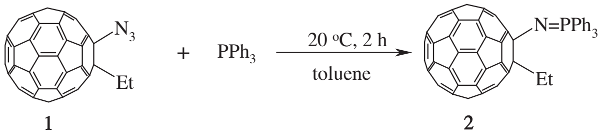
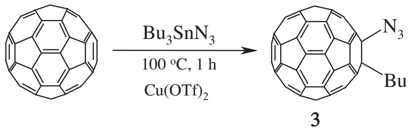


Figure 1. Long-range interactions of the methylene hydrogen atoms with the fullerene cage carbon atoms in the HMBC experiment.



Scheme 2.



Scheme 3.

All our attempts to react metal azides such as $Bu_2Sn(N_3)_2$ or $Na_2Sn(N_3)_6$ with fullerene C_{60} failed. Each experiment resulted in recovery of the initial fullerene.

According to thermal stability measurements of azidofullerenes **1** and **3**, refluxing these compounds in 1,2-dichlorobenzene resulted in an insoluble black precipitate, which was difficult to characterize. This precipitate is, in our opinion, an oligomer formed via intermolecular reaction of the starting azidofullerenes. Meanwhile, refluxing compounds **1** and **3** in toluene or chlorobenzene, even for a long period of time (10–15 h), did not induce thermal decomposition or further transformations.

In conclusion, we have reported for the first time the one-step synthesis of stable 1-azido-2-alkylfullerenes by the reaction of organometallic azides [Et_2AlN_3, $EtAl(N_3)_2$, Bu_3SnN_3] with fullerene C_{60} under thermal and catalytic reaction conditions.

Acknowledgement

This work was supported financially by the Russian Foundation for Basic Research (Project 12-03-31023).

References and notes

1. Wang, N.; Li, J.; Zhu, D. *Tetrahedron Lett.* **1995**, *36*, 431–434.
2. Yamakoshi, Y. N.; Yagami, T.; Sueyoshi, S.; Miyata, N. *J. Org. Chem.* **1996**, *61*, 7236–7237.
3. Gonzalez, S.; Martin, M.; Swartz, A.; Guldi, D. M. *Org. Lett.* **2003**, *5*, 557–560.
4. Sinyashin, O. G.; Romanova, I. P.; Yusupova, G. G.; Kovalenko, V. I.; Yanilkin, V. V.; Azancheev, N. M. *Mendeleev Commun.* **1999**, 96–98.
5. Akhmetov, A. R.; Tuktarov, A. R.; Dzhemilev, U. M.; Yarullin, I. R.; Gabidullina, L. A. *Russ. Chem. Bull.* **2011**, *9*, 1885–1887.
6. Dzhemilev, U. M.; Tuktarov, A. R.; Yarullin, I. R.; Akhmetov, A. R. *Mendeleev Commun.* **2013**, *23*, 326–328.
7. Rawal, V. H.; Zhong, H. M. *Tetrahedron Lett.* **1994**, *35*, 4947–4950.
8. Saito, S.; Yamashita, S.; Nishikawa, T.; Yokoyama, Y.; Inaba, M.; Moriwake, T. *Tetrahedron Lett.* **1989**, *30*, 4153–4156.
9. *Procedure for the synthesis of 1-azido-2-ethyl(C_{60}-I_h)[5,6]fullerene (**1**).* In a two-necked glass reactor, C_{60} (20 mg, 0.0277 mmol) was dissolved in anhydrous toluene (20 mL). The solution was cooled to −20 °C and a solution of Et_2AlN_3 or $EtAl(N_3)_2$ (0.1385 mmol) in toluene (2 mL) was added with vigorous stirring.[7] The cooling bath was removed and the mixture was heated to 40 °C, and stirring was continued for an additional 3 h. All experiments were carried out under a dry argon flow. After the reaction was complete, the mixture was quenched with 5% HCl, and the organic phase was separated and passed through a short silica gel layer. The reaction product **1** and unreacted C_{60} were separated by preparative HPLC using toluene as the eluent. This gave 1-azido-2-ethyl(C_{60}-I_h)[5,6]fullerene (**1**) in 20% yield as a brown powder.
10. *1-Azido-2-ethyl(C_{60}-I_h)[5,6]fullerene (**1**).* IR: 526, 552, 754, 1110, 1632, 2092, 2853, 2924 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 255, 315, 428. ^1H NMR (400.13 MHz, $CDCl_3$:CS_2 1:5): δ 3.66 (q, 2H, CH_2, $J = 7.2$ Hz), 2.06 (t, 3H, CH_3, $J = 7.2$ Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$:CS_2 1:5): δ 14.85, 34.92, 65.93, 79.91, 134.65, 136.62, 139.43, 139.78, 141.19, 141.28, 141.73, 142.05, 142.12, 142.14, 142.46, 142.58, 142.92, 144.12, 144.39, 144.68, 145.11, 145.16, 145.31, 145.46, 146.06, 146.09, 146.10, 146.27, 146.50, 147.58, 148.16, 148.99, 155.34. MALDI TOF, found: m/z 749.040 $[M-N_3]^-$; $C_{62}H_5$; calculated: M = 791.048 m/z $C_{62}N_3H_5$.
11. *Procedure for the synthesis of 1-N,P,P,P-triphenylphosphine imide-2-ethyl (C_{60}-I_h)[5,6]fullerene (**2**).* A two-necked glass reactor was charged with a

solution of **1** (10 mg, 0.012 mmol) in dry toluene (20 mL). Under a stream of dry argon at room temperature, and with vigorous stirring, PPh_3 (4.3 mg, 0.018 mmol) was added. Stirring was continued for 2.5 h in the dark. After the reaction was complete, the solvent was evaporated under reduced pressure and the residue washed with dry Et_2O (3×2 mL) and dried to give compound **2** in a quantitative yield.

12. *1-N,P,P,P-Triphenylphosphine imide-2-ethyl(C_{60}-I_h)[5,6]fullerene (**2**).* IR: 526, 542, 721, 1181, 1379, 1436, 2851, 2923 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 256, 314, 431. ^1H NMR (400.13 MHz, $CDCl_3$:CS_2 1:5): δ 2.06 (t, 3H, CH_3, $J = 7.2$ Hz), 3.66 (q, 2H, CH_2, $J = 7.2$ Hz), 7.45–7.6 (m, 3H, 3CH), 7.6–7.7 (m, 6H, 6CH), 8.0–8.12 (m, 6H, 6CH). ^{13}C NMR (100.62 MHz, $CDCl_3$:CS_2 1:5): δ 14.90, 34.96, 65.93, 79.89, 128.6 (d, $^2J_{P-C} = 12.07$), 131.89 (d, $^3J_{P-C} = 10.06$), 132.93 (d, $^1J_{P-C} = 45.28$), 141.20, 141.74, 142.06, 142.12, 142.15, 142.47, 142.59, 142.90, 142.93, 144.12, 144.40, 144.68, 145.11, 145.17, 145.31, 145.46, 146.07, 146.09, 146.10, 146.27, 146.50, 148.99, 155.34. MALDI TOF, found: m/z 1025.208 [M]; calculated: m/z 1025.995; $C_{80}H_{20}NP$; m/z 996.137 $[M-C_2H_5]^+$; $C_{78}H_{15}NP$.
13. *Procedure for the synthesis of 1-azido-2-butyl(C_{60}-I_h)[5,6]fullerene (**3**).* In a two-necked glass reactor, C_{60} (20 mg, 0.0277 mmol) was dissolved in anhydrous chlorobenzene (4 mL), and a solution of Bu_3SnN_3 (0.0554 mmol) in chlorobenzene (1 mL) and $Cu(OTf)_2$ (10 mg, 0.0277 mmol) were added with vigorous stirring. The mixture was heated to 100 °C over 1 h with stirring under a dry argon flow. After the reaction was complete, the mixture was quenched with 5% HCl, and the organic phase separated and passed through a short silica gel layer. The reaction product **3** and C_{60} were separated by preparative HPLC using toluene as the eluent. This gave 1-azido-2-butyl(C_{60}-I_h)[5,6]fullerene (**3**) in 30% yield as a brown powder.
14. *1-Azido-2-butyl(C_{60}-I_h)[5,6]fullerene (**3**).* IR: 527, 553, 574, 747, 1035, 1227, 2090, 2854, 2866, 2924, 2953 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 257, 319, 430. ^1H NMR (400.13 MHz, $CDCl_3$:CS_2 1:5): δ 3.56 (t, 2H, CH_2, $J = 7.6$ Hz), 2.51 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 1.29 (t, 3H, CH_3, $J = 7.6$ Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$:CS_2 1:5): δ 14.82, 24.40, 33.04, 41.75, 65.72, 80.16, 134.78, 136.92, 139.72, 140.12, 141.48, 141.56, 142.02, 142.34, 142.40, 142.44, 142.75, 142.88, 143.19, 144.43, 144.68, 144.97, 145.36, 145.38, 145.41, 145.60, 145.75, 146.36, 146.39, 146.54, 146.78, 147.86, 148.43, 149.27, 155.94. MALDI TOF, found: m/z 777.067 $[M-N_3]^-$; $C_{64}H_9$; calculated: M = 819.776 m/z $C_{64}N_3H_9$.