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The reaction of fullerene C_{60} with halogen azides

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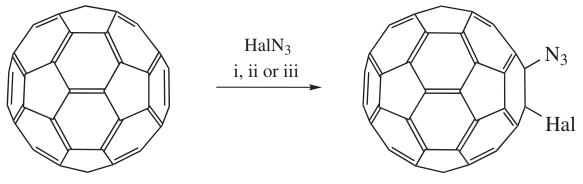
Reaction of fullerene C_{60} and halogen azides (IN_3, BrN_3) gives 1-halo-2-azidofullerenes, whose structures were proved by NMR and IR spectroscopy, MALDI-TOF mass spectrometry, and by their chemical transformations.

The reactions of fullerenes with organic azides attract significant attention due to the possibility to obtain functionally substituted compounds of interest to the medicine and engineering.[1,2] At present, the reactions of C_{60} with organic azides leading to triazolinofullerenes ([2+3]-cycloadducts),[3] 5,6- and 6,6-azahomofullerenes or 5,6- and 6,6-aziridinofullerenes ([2+1]-cycloadducts),[4] are thoroughly studied. Meantime, there has been no information about the reaction of fullerenes with inorganic azides, the implementation of which may result in previously unreported fullerene azides. We have earlier shown that the reaction between C_{60} and hydrazoic acid (HN_3) affords unsubstituted aziridinofullerene or triazolinofullerene depending on the reaction conditions.[5]

Here, we report the results of our further investigations into the reaction of C_{60} with halogen azides (IN_3, BrN_3). The effect of reaction conditions and the molar ratio of reactants on yields and composition of the reaction products were studied on the example of IN_3. In fact, on using three-fold excess of freshly prepared IN_3 under optimized conditions (–20 °C, 3 h, chlorobenzene) 1-iodo-2-azido(C_{60}-I_h)[5,6]fullerene **1** was obtained in 30% yield (Scheme 1).[†] Prolongation in the reaction time from 3 to 6–12 h leads to a formation of polyaddition products in the form of brown poorly soluble precipitate exploding on trituration. Compound **1** was isolated by preparative HPLC (Cosmosil Buckyprep column) and its structure was reliably established by standard analytical [1D and 2D NMR, IR, UV, MS (MALDI-TOF)] methods. IR spectrum of adduct **1** contains strong absorption bands at 2092, 1420, 1080, 620 and 463 cm^{-1}, belonging to the vibrations of the N_3 bonds, the fullerene core and the carbon–iodine bond, respectively. The MALDI-TOF mass spectrum contains the molecular ion peak of low intensity with *m*/*z* 889.920 (for $C_{60}N_3I$, *ca.* 889.584) and three peaks of average intensity with *m*/*z* 734.022 $[C_{60}N]^+$, 748.030 $[C_{60}N_2]^+$ and 762.027 $[C_{60}N_3]^+$. ^{13}C NMR spectrum of compound **1** is characterized by signals at δ_C 130–150 ppm belonging to sp^2-hybridized carbon atoms of the fullerene core. Unfortunately, we could not register the sp^3-hybridized C_{60} carbon atom associated with the azide group and the iodine atom because of low solubility of 1-iodo-2-azidofullerene **1** in organic solvents, and the low signal intensity of the fullerene carbon atoms, to which heteroatoms are attached.



1 Hal = I
2 Hal = Br

Scheme 1 *Reagents and conditions*: i, IN_3, –20 °C, PhCl, 3 h; ii, BrN_3, –40 °C, 3 h; iii, NBS, $TMSN_3$, $M(OTf)_n$, 20 °C, 1 h.

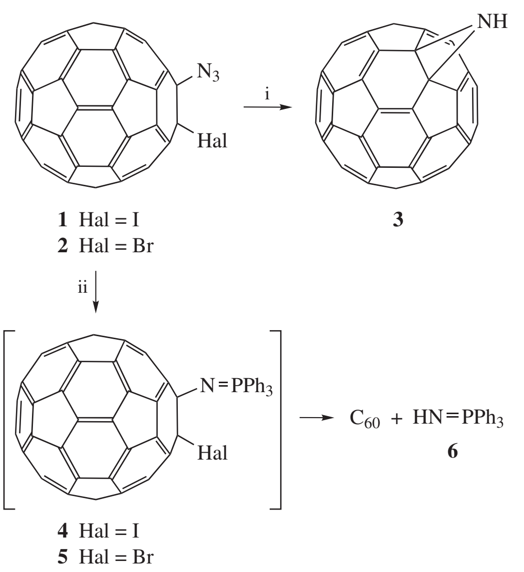
Analogously, bromine azide (–40 °C, 3 h, chlorobenzene) adds to C_{60} giving the corresponding bromoazidofullerene **2** (see Scheme 1). Taking into account the explosive characteristics of individual halogen azides, BrN_3 was also generated *in situ* from *N*-bromosuccinimide and trimethylsilyl azide in the presence of equimolar amounts of lanthanide (Sm, Yb, La) or copper triflates as catalysts.[6] In this case, 1-bromo-2-azidofullerene **2** was obtained in 30% yield.[‡]

To prove more reliably the structure of azido halo adducts **1** and **2**, some typical of organic azides chemical transformations were carried out. Their reduction with 1 M solution of BH_3·THF

[†] *1-Iodo-2-azido(C_{60}-I_h)[5,6]fullerene* **1**. A two-necked glass reactor, cooled to –20 °C was charged with a solution of 20 mg (0.0277 mmol) of C_{60} in 4 ml of dry chlorobenzene and 0.213 ml (0.0831 mmol) of freshly prepared IN_3 solution in chlorobenzene with vigorous stirring [IN_3 solution was prepared at –20 °C immediately before the synthesis from freshly distilled 0.078 ml (1.56 mmol) ICl and 200 mg (3.1 mmol) NaN_3 in 4 ml of dry chlorobenzene for 30 min]. The reaction mixture was stored in the dark at –20 °C for 3 h. All experiments were carried out in a stream of dry argon. Excess dry finely powdered $Na_2S_2O_3$ was then added, and the mixture was stirred for additional 5 min and then filtered. Product **1** and fullerene C_{60} were separated by preparative HPLC with toluene as an eluent. Yield of **1** was 30%. IR (ν/cm^{-1}): 463, 527, 543, 1037, 1218, 2092. UV ($CHCl_3$, λ_{max}/nm): 260, 319, 423. ^{13}C NMR [100 MHz, toluene-d_8–CS_2 (1:10)] δ: 139.53, 141.26, 141.57, 141.98, 142.40, 142.49, 142.60, 142.69, 143.76, 144.30, 145.11, 145.61, 145.87, 146.05, 146.35, 147.11, 147.46, 148.16, 148.43. MS (MALDI-TOF), *m*/*z*: 889.920 $[M]^+$ ($C_{60}IN_3$), 762.027 $[M-I]^+$ ($C_{60}N_3$), 748.030 $[M-IN]^+$ ($C_{60}N_2$), 734.022 $[M-IN_2]^+$ ($C_{60}N$).

[‡] *1-Bromo-2-azido(C_{60}-I_h)[5,6]fullerene* **2**. To a solution of 30 mg (0.042 mmol) of C_{60} in 6 ml of dry chlorobenzene in two-necked reactor at room temperature, trimethylsilyl azide (0.1 ml, 0.754 mmol), $Sm(OTf)_3$ (25 mg, 0.042 mmol) and *N*-bromosuccinimide (9 mg, 0.051 mmol) were sequentially added with vigorous stirring. The reaction mixture was stirred for 1 h in the dark in a stream of dry argon. After a time, 10 ml of toluene was added, the reaction mixture was passed through the column with a small amount of microcrystalline cellulose. Product **2** and C_{60} were separated by preparative HPLC with toluene as an eluent (or the reaction mixture was used without separation for the following experiments). Yield of **2** was 30%. IR (ν/cm^{-1}): 527, 542, 577, 752, 1035, 1220, 2096. UV ($CHCl_3$, λ_{max}/nm): 256, 319, 421. ^{13}C NMR [100 MHz, $CDCl_3$–CS_2 (1:5)] δ: 139.92, 140.82, 142.01, 143.02, 143.40, 143.74, 143.82, 144.12, 144.46, 144.62, 144.97, 145.40, 146.87, 145.78, 147.12, 147.27, 147.32, 148.15, 148.53, 148.59, 148.64, 148.77, 149.29, 149.43, 150.82, 154.46. MS (MALDI-TOF), *m*/*z*: 843.064 $[M]^+$ ($C_{60}BrN_3$), 762.025 $[M-Br]^+$ ($C_{60}N_3$), 748.020 $[M-BrN]^+$ ($C_{60}N_2$), 734.004 $[M-BrN_2]^+$ ($C_{60}N$).

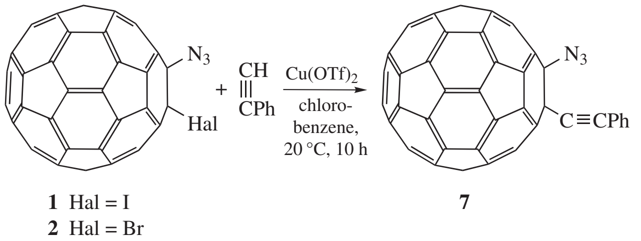
or gaseous NH_3 at room temperature for 12 h provided corresponding N-unsubstituted aziridinofullerene **3** in quantitative yield (Scheme 2). Note that $LiAlH_4$, $NaBH_4$, $N_2H_4{\cdot}H_2O$ or molecular H_2 in the presence of 10% Pd/C did not lead to compound **3**. The structure of **3** was proved by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and also by comparing the physical and chemical constants of the obtained sample with the literature data.[5,§]



Scheme 2 *Reagents and conditions*: i, $BH_3{\cdot}THF$ or NH_3, 12 h, –20 → 20 °C, HCl; ii, PPh_3, CH_2Cl_2, 20 °C.

The reaction of haloazidofullerenes **1** and **2** with PPh_3 in dry CH_2Cl_2 at room temperature afforded iminophosphoranes **4** and **5** (see Scheme 2),[§] which are extremely unstable compounds and underwent fragmentation into fullerene and iminophosphorane **6**, even during recording ^{13}C NMR spectra. The formation of **4** and **5** was proved by MALDI-TOF mass spectra, which contain the intense peaks at *m/z* 996, attributed to fragmentary ions $[M-I]^+$ and $[M-Br]^+$. The formation of iminophosphorane **6** as a result of decomposition of adducts **4** and **5** was also confirmed by ^1H, ^{13}C, ^{31}P NMR and GCMS spectra. Note that substituted stable iminophosphorane of fullerene was described in the literature.[7]

The reaction of azides with acetylenes leading to corresponding triazoles ('click chemistry'),[8,9] has recently become popular in fullerene chemistry.[10,11] In this regard, of great interest is to study the chemical behaviour of compounds **1** and **2** obtained in the reaction with acetylene, in particular, the ability of the azide group to form the corresponding triazoles. However, our experiments showed that azido group of compounds **1** and **2** did not react with phenylacetylene in the presence of $CuSO_4{\cdot}5H_2O$ and sodium ascorbate, as expected.[10,11] That may be due to steric hindrance, which create the bulky fullerene molecule and the halogen atom located near to the azide group. The optimization revealed that the reaction of **1** and **2** with a five-fold excess of phenylacetylene in the presence of equimolar amounts of $Cu(OTf)_2$ as a catalyst affords the Sonogashira[12] adduct **7** in quantitative yield (Scheme 3).[¶]



Scheme 3

The mass spectrum of compound **7** contains a molecular ion peak at *m/z* 863.040 (for $C_{68}N_3H_5$ *ca.* 863.801), and the fragmentary ions peaks at *m/z* 849.040, 835.030 and 821.025 due to $[C_{68}N_2H_5]^-$, $[C_{68}NH_5]^-$ and $[C_{68}H_5]^-$, respectively. The ^{13}C NMR spectrum of **7** has a set of 21 signals in the region 138–150 ppm, belonging to the sp^2-hybridized carbon atoms of the fullerene core. The sp^3-hybridized carbon atoms of the fullerene core resonate at δ_C 71.99 and 82.29 ppm and bound to the acetylene fragment and the azide group, respectively. A set of six signals (δ_C 85.47, 87.55, 128.12, 129.23, 131.70, 130.23) characterizes the acetylenic C≡C bond and the phenyl substituent. The intense band at 2097 cm^{-1} in the IR spectrum of compound **7** indicates the presence of the azide group in the C_{60} molecule.

To conclude, previously undescribed 1-halo-2-azidofullerenes have been synthesized by the reaction between fullerene C_{60} and halogen azides for the first time. The chemical structure of the synthesized azidofullerenes has been reliably established by physicochemical methods, and by means of some chemical transformations of azidofullerenes involving the carbon–nitrogen and the carbon–halogen bonds.

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[§] *Aziridino[2',3':1,2]fullerene[60]* **3**. The two-necked glass reactor was charged with a solution of **1** or **2** (10 mg, 0.011 mmol) in 4 ml of dry chlorobenzene. In a stream of dry argon at room temperature and with vigorous stirring, 1 M solution of $BH_3{\cdot}THF$ (1 ml, 1 mmol) was added. After 12 h, the reaction mixture was quenched with 5% HCl solution. After addition of toluene (7 ml) the organic layer was passed through the column with a small amount of silica gel to give product **3** in quantitative yield. A similar result was obtained by passing ammonia gas through solutions of **1** or **2** at –20 °C for 1 h. Then, the ammonia flow was stopped, the cooling was removed, and the mixture was left for 12 h at room temperature. 5% HCl solution of hydrochloric acid was added with vigorous stirring. After addition of toluene (7 ml), the organic layer was passed through the column with a small amount of silica gel to afford compound **3** in quantitative yield. Compound **3** was identified by comparison of its spectral characteristics with those described in literature.[5]

*1-Halo-2-[*N*-(triphenylphosphoranylidene)amino](C_{60}-I$_h$)[5,6]fullerenes* **4** *and* **5**. The two-necked glass reactor was charged with a solution of **1** or **2** (10 mg, 0.011 mmol) in 20 ml of dry CH_2Cl_2. In a stream of dry argon at room temperature and with vigorous stirring PPh_3 (4 mg, 0.0165 mmol) was added. Stirring was continued in the dark for 2.5 h. After the reaction was complete, the solvent was evaporated under reduced pressure, the residue was washed with dry diethyl ether (3×2 ml) to give unstable compounds **4** and **5**. MS (MALDI-TOF), *m/z*: 996.150 $[M-Hal]^+$ ($C_{78}PNH_{15}$).

[¶] *1-Azido-2-phenylethynyl(C_{60}-I$_h$)[5,6]fullerene* **7**. The two-neck glass reactor was charged with a solution of 0.035 mmol of compounds **1** or **2** in 6 ml of dry chlorobenzene. In a stream of dry argon at room temperature and with vigorous stirring 0.023 ml (0.178 mmol) of phenylacetylene and 12.6 mg (0.035 mmol) of $Cu(OTf)_2$ were added and the mixture was stirred for 10 h in the dark. Toluene (10 ml) was then added, and the mixture was passed through the column with a small amount of microcrystalline cellulose. The components were separated by preparative HPLC with toluene as the eluent. Product **7** was obtained in quantitative yield. IR (ν/cm^{-1}): 527, 558, 590, 756, 1103, 1219, 2097, 2237. UV ($CHCl_3$, λ_{max}/nm): 260, 317, 426. ^1H NMR [400 MHz, $CDCl_3$–CS_2 (1:5)] δ: 7.65 (m, 3H, 3CH), 8.01 (d, 2H, 2CH, *J* 6.4 Hz). ^{13}C NMR [100 MHz, $CDCl_3$–CS_2 (1:5)]: 71.99, 82.29, 85.47, 87.55, 128.12, 129.23, 130.11, 131.70, 140.97, 141.18, 141.62, 141.97, 142.30, 142.88, 142.94, 143.65, 143.82, 144.09, 144.35, 144.67, 144.89, 145.22, 145.34, 148.18, 148.87, 150.01, 150.74. MS (MALDI-TOF), *m/z*: 863.040 $[M]^-$ ($C_{68}N_3H_5$), 849.040 $[M-N]^-$ ($C_{68}N_2H_5$), 835.030 $[M-N_2]^-$ ($C_{68}NH_5$), 821.025 $[M-N_3]^-$ ($C_{68}H_5$).

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