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Cycloaddition of alkyl azides to fullerene C_{60} in the presence of $Cu(OTf)_2$

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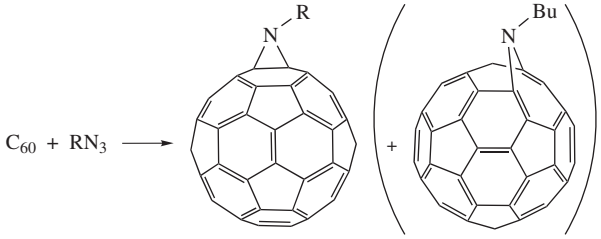
Cycloaddition of linear and cyclic alkyl azides to fullerene C_{60} in the presence of stoichiometric amounts of copper triflate affords *N*-(cyclo)alkylaziridinofullerenes.

Reactions of fullerenes with organic azides[1–3] serve as a good access to new functionally substituted carbon clusters. Thermal reactions between fullerene C_{60} and organic azides[3–6] proceed as 1,3-dipolar cycloaddition with the initial formation of fulleratriazolines. Subsequent extrusion of a nitrogen molecule from the triazoline cycle leads to mixtures of cycloadducts with predominant formation of open-5,6 (5,6-azahomofullerenes)[7,8] or [2+1]-closed (5,6- or 6,6-aziridinofullerenes)[9,10] isomers. Such thermal processes are difficult to control. A new efficient protocol[11] was proposed recently to produce aziridino[5,6]-fullerenes through the Lewis acid-assisted decomposition of triazolinofullerenes obtained by thermal addition of azides to C_{60}. The main disadvantage of this protocol is the necessity for isolation of intermediate triazolinofullerenes as well as the employment of aggressive trifluoromethanesulfonic acid or boron compounds.

By the beginning of our research, data on coupling of organic azides and carbon clusters in the presence of salts and complexes of transition metals and rare earth elements were lacking. Meanwhile, the alternative methods to produce aziridinofullerenes, including those mediated by metal salts and complexes, were previously described.[12–14]

Recently, we have performed the first study of the reactions of C_{60} with inorganic (HN_3, IN_3, BrN_3)[15,16] and organometallic [Et_2AlN_3, $EtAl(N_3)_2$ and Bu_3SnN_3][17] azides leading to azidofullerenes. Also, we have succeeded in developing cycloaddition reactions between C_{60} and various diazo compounds under the action of palladium–phosphine complexes.[18] In continuation of these studies, herein we report on addition of fullerene C_{60} to organic azides in the presence of transition and rare earth elements.

On application of model butyl azide, we found that Cu, La, Sm and Yb triflates exhibit the highest activity among the tested transition and rare earth metal complexes (Scheme 1, Table 1). In general, the two products, aziridinofullerene **2** and azahomofullerene **3**, were formed. The optimal amount of metal promoter



1a R = Bu **1e** R = C_9H_{19}
1b R = Me **1f** R = cyclohexyl
1c R = Et **1g** R = cyclooctyl
1d R = Pr^i

Scheme 1

Table 1 Effect of metal complex structure on the ratio of cycloadducts **1a** and **2a**.[a]

Metal complexes	Conversion of C_{60} (%)	Ratio **1**:**2**
$Cu(OTf)_2$	30	1:0
$La(OTf)_3$	20	1:0
$Sm(OTf)_3$	18	1:0
$Yb(OTf)_3$	15	1:0
$Pd(PPh_3)_4$	25	9:1
CuCl	11	1:2
$Pd(PPh_3)_2Cl_2$	10	1:9
$Rh(acac)_3$	10	1:2
$PdCl_2$	15	1:1

[a] Conditions: freshly prepared butyl azide and C_{60} (1:1 molar ratio), 100 mol% of $M(OTf)_n$, 100 °C, 3 h, chlorobenzene.

was 100 mol%; its lowering caused dropping in conversion and selectivity. The best of promoters turned to be $Cu(OTf)_2$.

At lower temperatures, the reaction time significantly increased, for example, at ambient temperature the same yield of the target product was achieved within one week. The replacement of chlorobenzene by other solvents such as dichlorobenzene, trichlorobenzene or tetrachloroethane had no effect on the yield and composition of the products. When using toluene or benzene as solvents, the yield of the cycloadduct **1a** reduced from 30 to 15% that was probably due to partial deactivation of the nitrene. In the absence of a catalyst, this reaction led to a 1:4 mixture of 6,6-aziridino- **1a** and 5,6-azahomofullerenes **2a** in 15% total yield (Scheme 1).

Compound **1** and the mixture of cycloadducts **1a** and **2a** were isolated by preparative HPLC and characterized by IR, UV, one-dimensional (^1H, ^{13}C) and two-dimensional (HHCOSY, HSQC, HMBC) NMR spectroscopy, MALDI TOF mass spectrometry.

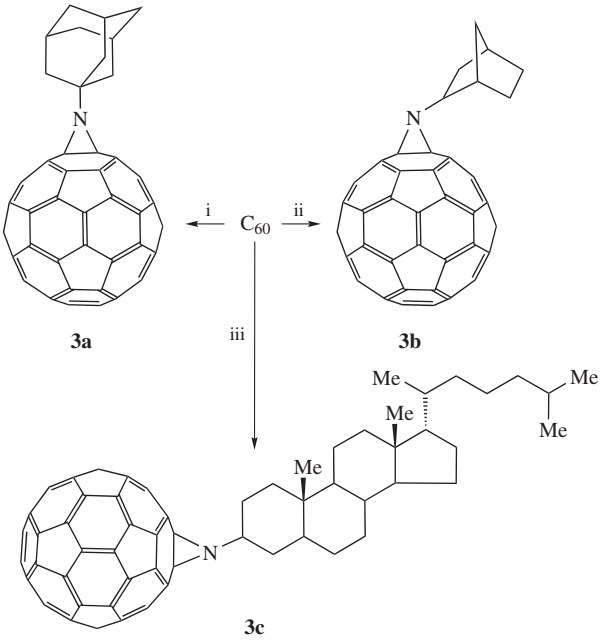
The NMR spectra of aziridinofullerene **1a** are fully consistent with the literature data.[11] Unfortunately, our attempts to isolate 5,6-azahomofullerene **2a** in pure form failed.

In a similar fashion, other organic azides were subjected to $Cu(OTf)_2$-catalyzed reaction with C_{60} affording the corresponding 6,6-aziridinofullerenes **1b**–**g**† in 27–40% yields (see Scheme 1).

† *Synthesis of* N-*alkylaziridino*(C_{60}-I_h)[5,6]*fullerenes (general procedure).* In a two-necked glass reactor, C_{60} (40 mg, 0.055 mmol) was dissolved in anhydrous chlorobenzene (8 ml). Then organic azide (0.055 mmol) and $Cu(OTf)_2$ (20 mg, 0.055 mmol) were added with vigorous stirring. The reaction mixture was heated up to 100 °C on stirring for additional 3 h. All experiments were carried out under a dry argon flow. After the reaction was complete, the mixture was passed through a short silica gel layer. The products and unreacted C_{60} were separated by preparative HPLC using toluene as the eluent. The NMR spectra of compounds **1a**,**b** were identical to those described in the literature.[11]

The data obtained indicate that the structure of the azide has little effect on the yield and direction of the cycloaddition. In the case of bulky cycloalkyl azides the yields of the adducts **1f**,**g** were somewhat lower.

The encouraging results on the catalytic synthesis of 6,6-aziridinofullerenes containing linear and simple cyclic substituents inspired us to extend the scope of the developed method onto more complex organic azides (Scheme 2).‡ The corresponding conjugated aziridinofullerenes **3a–c**‡ were obtained in 20–40% yield (Scheme 2).



Scheme 2 *Reagents*: i, 1-azidoadamantane; ii, 2-azidonorbornene; iii, 3-azidocholestane.

N-*Methylaziridino[2',3':1,9](C$_{60}$-I$_h$)[5,6]fullerene* **1b**:[11] yield 28%.

N-*Isopropylaziridino[2',3':1,9](C$_{60}$-I$_h$)[5,6]fullerene* **1d**: yield 40%. IR (ν/cm^{-1}): 526, 572, 755, 1170, 1631, 2853, 2923. UV ($CHCl_3$, λ_{max}/nm): 325, 424. ^{1}H NMR (500.17 MHz, $CDCl_3$–CS_2 1:5) δ: 1.79 (d, 6H, 2Me, *J* 6 Hz), 3.75 (m, 1H, CH). ^{13}C NMR (125.76 MHz, $CDCl_3$–CS_2 1:5) δ: 21.76, 51.59, 85.51, 140.88, 142.24, 142.40, 142.99, 143.16, 143.86, 144.52, 144.62, 144.70, 145.17, 145.21. MS (MALDI-TOF), *m*/*z*: 777.036 $[M]^-$ ($C_{63}NH_7$).

N-*Cyclohexylaziridino[2',3':1,9](C$_{60}$-I$_h$)[5,6]fullerene* **1f**: yield 30%. IR (ν/cm^{-1}): 526, 572, 755, 1185, 1629, 2852, 2926. UV ($CHCl_3$, λ_{max}/nm): 326, 424. ^{1}H NMR (500.17 MHz, $CDCl_3$–CS_2 1:5) δ: 1.60 (m, 2H, CH_2), 2.22–2.09 (m, 4H, 2CH_2), 2.42 (m, 4H, 2CH_2), 3.43 (m, 1H, CH). ^{13}C NMR (125.76 MHz, $CDCl_3$–CS_2 1:5) δ: 25.11, 26.69, 32.14, 58.47, 84.87, 140.87, 142.23, 142.42, 142.99, 143.15, 143.88, 144.53, 144.62, 144.69, 145.18, 145.22. MS (MALDI-TOF), *m*/*z*: 817.068 $[M]^-$ ($C_{66}NH_{11}$).

For characteristics of compounds **1c**,**e**,**g**, see Online Supplementary Materials.

‡ N-*(Adamantan-1-yl)aziridino[2',3':1,9](C$_{60}$-I$_h$)[5,6]fullerene* **3a**: yield 20%. IR (ν/cm^{-1}) 525, 572, 757, 1173, 1637, 2850, 2921. UV ($CHCl_3$, λ_{max}/nm): 258, 325, 428. ^{1}H NMR (500.17 MHz, $CDCl_3$–CS_2 1:5) δ: 1.92 (m, 6H, 3CH_2), 2.38 (m, 3H, 3CH), 2.60 (d, 6H, 3CH_2, *J* 2 Hz). ^{13}C NMR (125.76 MHz, $CDCl_3$–CS_2 1:5) δ: 30.63, 36.83, 42.53, 62.72, 85.07, 142.32, 142.34, 143.13, 143.16, 143.71, 144.25, 144.30, 144.54, 144.60, 144.96, 145.01. MS (MALDI-TOF), *m*/*z*: 869.163 $[M]^-$ ($C_{70}NH_{15}$).

N-*Norborn-2-ylaziridino[2',3':1,9](C$_{60}$-I$_h$)[5,6]fullerene* **3b**: yield 40%. IR (ν/cm^{-1}): 526, 571, 750, 1170, 1635, 2849, 2918. UV ($CHCl_3$, λ_{max}/nm): 256, 323, 421. ^{1}H NMR (500.17 MHz, $CDCl_3$–CS_2 1:5) δ: 1.6–1.7 (m, 4H, CH_2, 2CH), 1.8 and 2.22 (m, 5H, 2CH_2, CH), 2.54 (m, 7H, 3CH_2, CH), 2.7 (m, 5H, 2CH_2, CH), 2.8 (m, 4H, CH_2, 2CH), 3.98 (m, 4H, 2CH, CH_2). ^{13}C NMR (125.76 MHz, $CDCl_3$–CS_2 1:5) δ: 23.22, 36.73, 38.44, 39.33, 41.63, 61.44, 63.83, 86.11, 140.80, 140.83, 142.24, 142.40, 142.98, 143.15, 143.85, 144.48, 144.60, 144.65, 145.15. MS (MALDI-TOF), *m*/*z*: 829.105 $[M]^-$ ($C_{67}NH_{11}$).

In conclusion, we have developed a highly selective method for the cycloaddition of organic azides to fullerene C_{60} promoted by copper triflate, which opens up a fairly simple and effective pathway for the synthesis of the new individual practically important aziridinofullerenes with various substituents including those based on natural compounds.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.09.009.

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