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N-Fluorobenzenesulfonimide Based Functionalization of C_{60}

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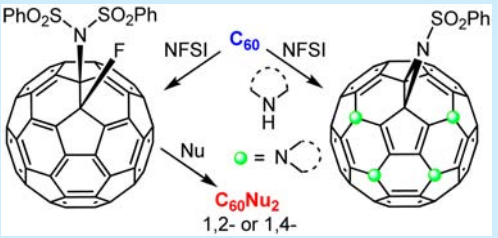
Supporting Information

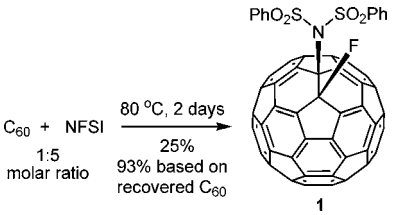
ABSTRACT: The reaction of *N*-fluorobenzenesulfonimide (NFSI) with C_{60} and exploration of the product as a precursor for various 1,2- and 1,4-bisfullerene adducts are reported. NFSI is also found to act as an oxidant in the reaction of C_{60} with cyclic amines such as pyrrolidine yielding tetraaminoaziridino adducts.



Selective functionalization of fullerenes has been one of the key research areas in fullerene chemistry.[1] New methods are still being explored actively.[2] Besides direct addition to pristine fullerenes, readily prepared fullerene derivatives have also been used as precursors for designed preparations of fullerene derivatives. For example, aziridinofullerenes have been shown to be a versatile platform for various fullerene derivatives.[3] Here we report the preparation of a monofluorinated C_{60} derivative and its application as an efficient synthon for selective preparation of C_{60} bisadducts, some of which cannot be prepared by other methods. In addition a novel type of tetraaminoaziridine C_{60} adduct has been prepared through *N*-fluorobenzenesulfonimide (NFSI) mediated amination.

Commercially available NFSI has been widely used as a mild electrophilic fluorination reagent.[4] Nucleophilic[5] and radical aminations[4e,6] have also been reported using NFSI as the nitrogen source. In an effort to prepare fluorofullerenes suitable for further functionalization, we investigated the reaction of NFSI with C_{60}. Following the literature procedure for fluorination of alkenes,[6a] we first treated C_{60} with NFSI and CuCl in *o*-dichlorobenzene. We hoped that fluorine radicals formed from the reduction of NFSI by CuCl would add to C_{60}. Indeed we were able to isolate compound **1** as the major product. We then started to optimize the reaction conditions by changing the solvent, temperature, reaction time, and molar ratio of reactants. To our surprise we found that the same product with the same yield could be obtained without the addition of CuCl. So a concerted 2 + 2 cycloaddition is probably operative for the formation of **1**. Homolysis of NFSI is unlikely without any metal catalyst, and we did not detect any bisfluoro- or multifluorofullerene. Heterolysis of NFSI would result in a higher activation energy than that of a concerted process. The reaction was stopped with a relatively low conversion of C_{60} (27%) to avoid formation of complex multiadducts. Under optimized conditions shown in Scheme 1, compound **1** was obtained in over 90% yield based on recovered C_{60} for reactions up to a 180 mg C_{60} scale.

Scheme 1. Addition of NFSI to C_{60}



The spectroscopic data for compound **1** are in agreement with the 1,2-adduct as depicted in Scheme 1. The ^{1}H NMR spectrum indicates the two phenyl groups are equivalent. The ^{13}C NMR spectrum showed the expected coupling of the fluorine atom to the fullerene cage carbons. The coupling constant for the fluorine bound sp^3 cage carbon is 203 Hz. The fluorine coupling constant for the neighboring imide bound sp^3 cage carbon is 25 Hz. A few signals in the sp^2 carbon region appear to be doublets, but they could not be assigned conclusively. The total number of sp^2 carbon signals is 37 counting all the doublets as two separate signals. Such a number suggests the 1,2-addition pattern with a C_s symmetry. A 1,4-addition pattern would be C_1 symmetric and would exhibit 58 sp^2 carbon signals.

Having compound **1** in hand we then explored its reactivity toward various nucleophiles. Toluene was tested as a representative of aromatic compounds. The 1,4-adduct compound **2**[7] was obtained by heating a mixture of compound **1** and *p*-toluenesulfonic acid (TsOH) at 100 °C in toluene (Table 1). A crude mixture of **1** containing some NFSI could be used for the reaction without affecting the overall yield. To simplify the procedure we used a crude mixture of **1** containing some NFSI for all further reactions and calculated the total yields for the two steps starting from C_{60} (Table 1). Methanol

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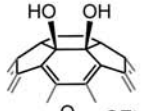
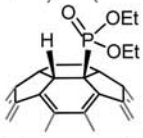
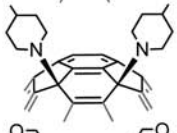
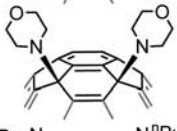
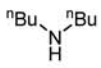
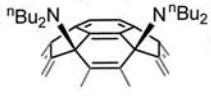
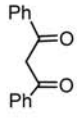
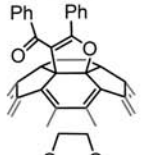
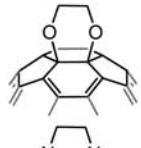
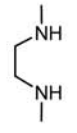
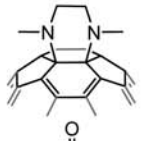
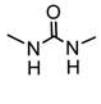
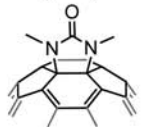
Table 1. Substitution Reactions of 1 with Nucleophiles

nucleophile	condition	product	yield[a] (brsm)
	TsOH 100 °C 30 min		**2** 19% (71%)
MeOH	TsOH 100 °C 5 h		**3** 21% (78%)
H_2O	TsOH 100 °C 48 h		**4** 10% (37%)
$P(OEt)_3$	TsOH 100 °C 30 min		**5** 9% (35%)
	35 °C 15 min		**6** 22% (81%)
	35 °C 15 min		**7** 18% (67%)
	35 °C 30 min		**8** 17% (64%)
	TsOH 100 °C 0.5 h		**9** 21% (78%)
	TsOH 100 °C 17 h		**10** 8% (29%)
	35 °C 5 min		**11** 20% (75%)
	TsOH 100 °C 5 h		**12** 5% (19%)

[a]Overall yield for two steps; brsm: based on recovered starting material C_{60}.

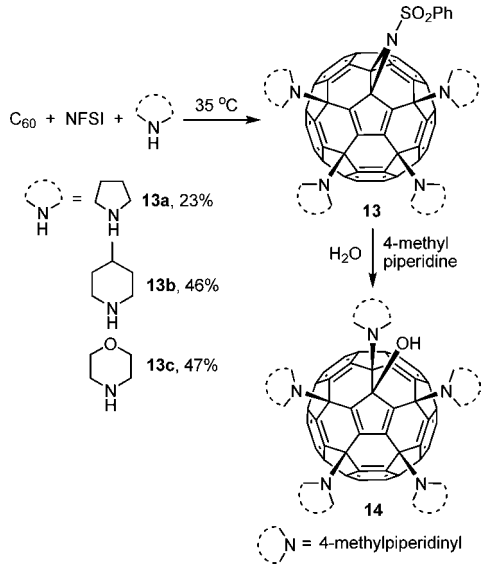
reacted similarly to give the 1,4-adduct **3**[8] with *o*-dichlorobenzene as the solvent. But the reaction with water yielded the 1,2-fullerenediol **4**.[9] Triethylphosphite yielded the 1,2-adduct **5**[10] under similar conditions. The more nucleophilic secondary amines 4-methylpiperidine, morpholine, and di-*n*-butylamine reacted directly with **1** without the addition of TsOH at a much lower temperature to give 1,4-adduct **6**, **7**,[11] and **8** respectively. These diamino fullerene adducts are less stable compared to compounds **2**−**5**. Compound **6** is disproportioned slowly into C_{60} and an unknown tetraamino adduct which could not be isolated but was present in the NMR spectra of **6** as a minor impurity and also appeared as a minor signal on the HRMS of **6**. Compound **8**, which cannot be prepared by known methods, readily reacts with 4-methylpiperidine to form **6** just like the interconversion reaction of 1,4-diaminofullerenes reported by Troshin et al.[12]

Nucleophiles with two possible reaction sites reacted with **1** to give 1,2-adduct exclusively (Table 1). Dibenzoylmethane reacted with **1** to give the dihydrofuran-fused fullerene product **9**. Both the yield of **9** and the reaction time are similar to those of the toluene adduct **2**, indicating similar reactivity. The formation of product **10**[13] from the reaction with 1,2-ethylenediol was much slower than that of methanol adduct **3**. But the reaction of **1** with *N*,*N*′-dimethylethylenediamine to form **11**[14] was much faster than those reactions with secondary amines. The 1,3-dimethylurea adduct **12** is quite unique. Under similar conditions other amides such as benzoyl amide did not give a characterizable product.[15] Sulfamides have been reported to form fullerene-fused diamination adducts through oxidation with $PhIO/I_2$.[16] Substitution of aziridinofullerene by urea can also produce imidazolinofullerenes analogous to **12**.[17]

As mentioned above a mixture of **1** and some unreacted NFSI were used for the preparation of the above compounds. The procedure for the two-step process is a pseudo-one-pot reaction since we used a short column to remove most of the unreacted starting materials and some polar impurities after the formation of compound **1**. To further improve the procedure, we tested the one-pot reaction conditions. Heating a mixture of C_{60}, NFSI, and TsOH in toluene did not give **2**, but only resulted in a complex mixture. Adding methanol to the *o*-dichlorobenzene solution of C_{60}, NFSI, and TsOH did not give the methanol adduct **3** either. Only the reaction with triethylphosphite gave the same product **5** with improved yield, from 9% under the two-step conditions to 21% under the one-pot conditions.

The attempted one-pot reaction for the cyclic secondary amines resulted in completely different products as shown in Scheme 2. The tetraaminoaziridino fullerene adducts **13a**−**c** were formed as the major product under optimized conditions from the reaction with pyrrolidine, 4-methylpiperidine, and morpholine, respectively. Secondary amines were added in a large excess (over 30 equiv). The amount of NFSI was crucial for the formation of the present aziridine containing adducts. The optimal amount is 5 equiv of NFSI for each mole of C_{60} in

Scheme 2. One-Pot Reaction to Form Multiamino Adducts



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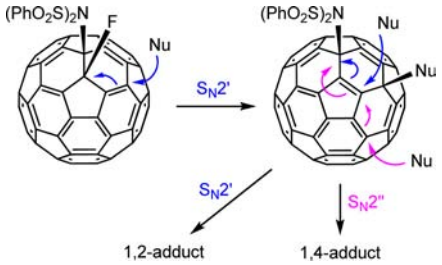
the preparation of **13a** and **13b**. More NFSI (10 equiv) was added for the less reactive morpholine to form **13c**. In a reaction with only 2 equiv of NFSI, we obtained the pentaaminohydroxyl adduct $C_{60}(OH)X_5$ (X = 4-methylpiperdinyl) **14** as the major product, which has been reported recently from the reaction of C_{60} with 4-methylpiperidine directly.[2a] Treating isolated **13b** with 4-methylpiperidine can also give **14**. The less reactive acyclic secondary amines such as dimethylamine and di-*n*-butylamine did not give any isolable product under the one-pot reaction conditions.

Compounds **13a–c** exhibit the typical C_s symmetric NMR spectra just like those for the well-known tetraamino epoxy C_{60} derivatives.[18] The ^{13}C NMR of the pyrrolidine derivative **13a** shows 4 sp^3 fullerene signals at 62.2, 67.2, 69.1, and 72.3 ppm in a 1:1:2:2 intensity ratio. There are 32 well resolved sp^2 signals for the fullerene cage and the phenyl group. The NMR spectra of compounds **13b** and **13c** show a similar pattern, but a few signals are broad due to steric hindrance. A similar signal broadening phenomenon has been observed before for analogous multiadducts.[2a] All the HRMS spectra of compounds **13a–c** showed the molecular ion signal as the most intensive signal.

Possible pathways for the double replacement of compound **1** to form the 1,2- or 1,4-adduct are shown in Scheme 3. The

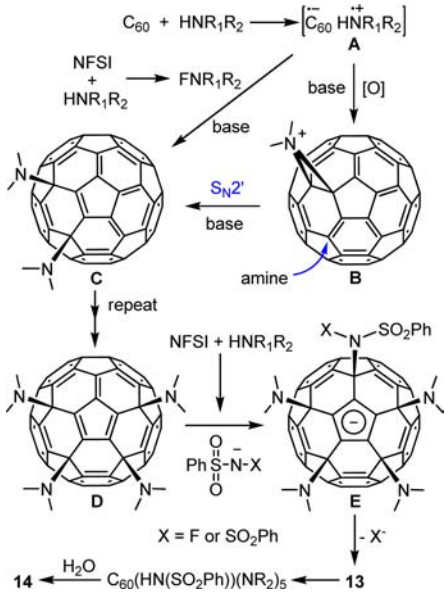
Scheme 3. Possible Mechanism for Double Substitutions



first S_N2' step probably replaces the fluorine to form the 1,4-adduct intermediate. The ESI mass spectrum showed only the signal for $[C_{60}N(SO_2Ph)_2]^+$, indicating the fluoride is probably a better leaving group. Depending on the steric hindrance the second nucleophile can replace the sulfonimide through either the S_N2' or S_N2'' to form the 1,2- and 1,4-adduct, respectively. For the weaker O and/or C nucleophiles, the catalyst TsOH is required which protonates the leaving groups to facilitate the substitution reactions. In the triethylphosphite reaction, electron transfer processes must be involved to form anionic fullerene intermediates, followed by protonation to form the 1,2-adduct **5**. The unique reduction property of triethylphosphite is probably responsible for the successful formation of **5** under both the stepwise and one-pot conditions. More reactive radical species may be formed through redox reaction between NFSI and triethylphosphite in the one-pot reaction to form **5** since the one-pot reaction required only 35 °C instead of 100 °C for the stepwise reaction. A trace amount of water in the solvent and in the TsOH hydrate hydrolyzes one of the ethoxyl groups in $P(OEt)_3$ in the formation of **5**.

The formation of the multiadducts **13a–c** may follow the pathway shown in Scheme 4. Even though the cyclic secondary amines can react with C_{60} themselves to form the tetraaminoepoxy adduct, the reaction needs oxygen and light or addition of an oxidant such as cumene hydroperoxide or DMSO.[18] Under the present one-pot conditions, NFSI may act

Scheme 4. Possible Pathway for the Formation of Multiamino Adducts



as the oxidant in the conversion from **A** to **B**. NFSI has been used as an oxidant for high valent metal centers in catalytic reactions.[19] The fulvalene moiety in **D** is active enough to react with the sulfonimide to form **E** with the aromatic cyclopentadienyl anion moiety, which gave the final product **13** by releasing the X^- on the imido nitrogen. The reaction between NFSI and excess secondary amine HNR_1R_2 may form either $(PhSO_2)_2N^-$ and FNR_1R_2 or $(PhSO_2)(F)N^-$ and $PhSO_2(NR_1R_2)$. NFSI has been reported as a phenylsulphonyl-group transfer instead of a fluorination reagent.[20] The other product FNR_1R_2 in the formation of $(PhSO_2)_2N^-$ may also act as the oxidant in the amination process or adds to an electron-rich amination intermediate such as the zwitterions **A** directly through an electrophilic amination process to form **C**. The analogous chloramine-T $(TsNCl)^-$ has been used as an efficient aziridination agent for C_{60} by refluxing in toluene.[21] In the presence of excess secondary amine and after an extended reaction time, the aziridine moiety in **13** can be opened to form $C_{60}(HN(SO_2Ph))(NR_2)_5$,[22] which then reacts with water or hydroxide through an S_N2' process to form **14** giving off the sulfonamide.

In summary the fluorinating reagent NFSI is found to act as both the fluoroamination electrophile to form the fluoroamination 1,2-adduct **1** and the oxidant in the reaction of secondary amines with C_{60}. Compound **1** serves as a versatile precursor for a series of 1,2- and 1,4-fullerene adducts with C, O, N, and P nucleophiles. The present NFSI mediated reactions afforded a few new fullerene derivatives which are difficult to be prepared by known methods. Further transformations of the novel tetraaminoaziridino adducts will be explored.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data, and copies of ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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