Synthesis of C_{60}-fused tetrahydrothiophene derivatives *via* nucleophilic cycloaddition of thiocyanates†

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Nucleophilic cycloaddition of thiocyanates **1a–e** with C_{60} in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene afforded C_{60}-fused 2-iminotetrahydrothiophene derivatives **2a–e** and methanofullerenes **3a–d**. The product distributions were highly sensitive to the substrates employed. The 2-iminotetrahydrothiophene derivatives **2a–e** could be further manipulated by hydrolysis and acetylation to give 2-oxotetrahydrothiophene derivatives **4a–e** and 2-acetamidotetrahydrothiophene derivatives **5a–e**. A possible reaction mechanism for the formation of products **2a–e** and **3a–d** was proposed.

Introduction

Since fullerenes became available in a macroscopic amount in 1990, various effective methods[1] have been developed to synthesize an impressive number of fullerene derivatives, which may find application in biology and material science.[2] Among them sulfur-containing fullerene derivatives demonstrate interesting electronic properties.[3] Fullerene diads and triads bearing oligothiophene/polythiophene[4] and tetrathiofulvalene/π-extended tetrathiofulvalene[5] have been intensively studied. Sulfur reagents such as sulfones,[4b,6] sultines,[7] stabilized sulfonium ylides,[8] α,β-unsaturated thiocarbonyl compounds,[9] *o*-thioquinone methide,[10] a thiocarbonyl ylide,[11] heterocyclic masked 1,3-dipoles 5-imino-1,2,4-thiadiazolidine-3-ones,[12] disulfides,[13] SO_3,[14] H_2S[15] and sulfur itself[16] have been employed in fullerene chemistry. Recently a new protocol for the synthesis of sulfur-containing dihydro-pyrrolo C_{60} derivatives was reported by Elemes and co-workers,[17] utilizing the 1,3-dipolar cycloaddition reaction of C_{60} with sulfide-bearing imines of glycine esters. We synthesized sulfur-containing C_{60} derivatives by the reaction of C_{60} with CS_2 and amino acid ester hydrochlorides in the presence of triethylamine (Et_3N).[18] Isothiocyanates generated *in situ* from amino acid ester hydrochlorides and CS_2 in the presence of Et_3N were believed to undergo subsequent nucleophilic cycloaddition with C_{60}. However, the reaction of thiocyanates with C_{60} has not been reported until now. In continuation of our interest in fullerene chemistry,[18,19] herein we disclose the nucleophilic cycloaddition of thiocyanates with C_{60}, affording C_{60}-fused 2-iminotetrahydrothiophene derivatives, and further transformations to other fullerene derivatives.

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† Electronic supplementary information (ESI) available: Spectral data of products **2a–e**, **3c**, **4a–e** and **5a–e**, and NMR spectra of representative products **2a**, **3c**, **4a** and **5a**. For ESI see DOI: 10.1039/b807394e

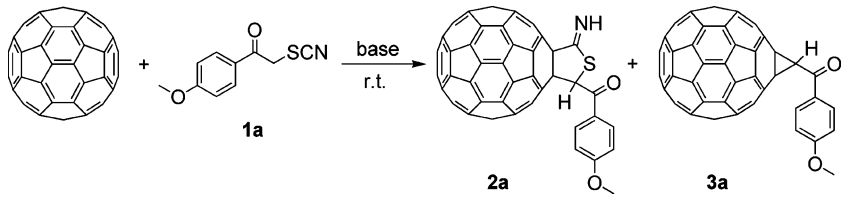
Results and discussion

Thiocyanates have been used in the synthesis of thiazole derivatives.[20] However, reactions employing the α-carbon of these compounds as a nucleophilic site are really rare.[21] We thus investigated the feasibility of the nucleophilic attack of the α-carbon of thiocyanates on C_{60} under basic conditions.

We chose the reaction of C_{60} with 1-(4-methoxyphenyl)-2-thiocyanatoethanone (**1a**) as a model reaction to optimize the reaction conditions (Scheme 1).

By using triethylamine, pyridine, 4-dimethylaminopyridine (DMAP) or triethylenediamine (DABCO) as a base, the reaction afforded products **2a** and **3a** (Scheme 1) in very low yields with over 90% recovered C_{60} (entries 1–4, Table 1). To our delight, the reaction proceeded rapidly to give products **2a** and **3a** in 65% total yield in 10 min when 1 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used. Product **3a** was obtained as the major product with a yield of 44%, being more than twice that (21%) of product **2a** (entry 5, Table 1). The structures of products **2a** and **3a** were assigned as a C_{60}-fused 2-iminotetrahydrothiophene derivative and a methanofullerene derivative, respectively (*vide infra*). Reducing the amount of DBU to 0.5 equiv., the total yield of the two products was almost the same with little change in the product distribution (entry 6, Table 1). Interestingly, further reducing the quantity of DBU to 0.2 equiv. led to the preferred formation of adduct **2a** (entry 7, Table 1). The product ratio of adduct **2a** *vs.* adduct **3a** increased to nearly 3 : 1 when 0.1 equiv. of DBU was employed (entry 8, Table 1). Nevertheless, an unsatisfactory result was obtained in terms of total yield and reaction time when 0.05 equiv. of DBU was applied (entry 9, Table 1). The above data demonstrated that the major product (adduct **2a** *vs.* adduct **3a**) could be altered by adjusting the amount of DBU used.

Being interested in the product type of adduct **2a**, we extended the reaction shown in Scheme 1 by replacing substrate **1a** with various types of thiocyanate and using the appropriate amount of DBU. Other 1-aryl-2-thiocyanatoethanones (**1b** and **1c**), thiocyanatoacetate (**1d**) and thiocyanatomalonate (**1e**) were explored for their reactions with C_{60} in the presence of DBU. It was found that the reaction of C_{60} with thiocyanates **1b–e** gave



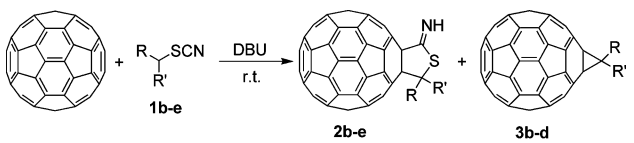
Scheme 1

Table 1 Product yields and recovered C_{60} for the reaction of C_{60} with **1a** under different reaction conditions [a]

Entry	Base	Equiv. of base	Time	Yield of **2a** [b]	Yield of **3a** [b]	Recovered C_{60}
1	Et_3N	1	24 h	2%	3%	91%
2	Pyridine	1	24 h	2%	2%	94%
3	DMAP	1	24 h	2%	3%	90%
4	DABCO	1	24 h	2%	3%	91%
5	DBU	1	10 min	21%	44%	19%
6	DBU	0.5	1 h	25%	39%	17%
7	DBU	0.2	4 h	34%	21%	25%
8	DBU	0.1	4 h	31%	11%	49%
9	DBU	0.05	12 h	13%	4%	74%

[a] 36.0 mg (0.05 mmol) of C_{60}, 20.7 mg (0.1 mmol) of **1a** were used, the reaction was conducted at room temperature. [b] Isolated yield.

both tetrahydrothiophene derivatives **2b–e** and methanofullerene derivatives **3b–d** except for **1e**, which afforded **2e** exclusively (Scheme 2).



Scheme 2

The yields of products **2a–e** and **3a–d**, along with recovered C_{60}, for the reaction of C_{60} with thiocyanates **1a–e** are listed in Table 2. As seen from Table 2, when R = H and R′ = Ar, the yields of products **2a–c** were more than 30%, while the yields of products **3a–c** were less than 12%, and the electronic properties of the substituent on the phenyl ring of the R′ group had little effect on the product yields. However, when R = H and R′ = $CO_2C(CH_3)_3$ (**1d**), product **2d** was obtained in a lower yield (13%), while the Bingel-type adduct **3d** was isolated in a slightly higher yield (18%). To our surprise, when diethyl 2-thiocyanatomalonate (**1e**) was employed, tetrahydrothiophene derivative **2e** was obtained selectively.

Table 2 The yields of products **2a–e** and **3a–d** for the reaction of C_{60} with **1a–e** in the presence of DBU at room temperature[a]

Substrate	Time (h)	Yield of **2** [b]	Yield of **3**[b]	Recovered C_{60}
1a	4	31%	11%	49%
1b	4	31%	11%	47%
1c	4	30%	12%	50%
1d[c]	12	13%	18%	60%
1e[d]	12	32%	0	64%

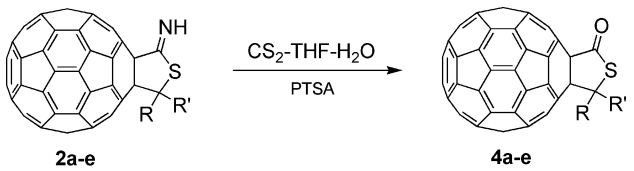
[a] Unless specified, the molar ratio of C_{60} : **1** : DBU = 1 : 2 : 0.1. [b] Isolated yield. [c] Molar ratio of C_{60} : **1d** : DBU = 1 : 2 : 0.2. [d] Molar ratio of C_{60} : **1e** : DBU = 1 : 2 : 1.

The structures of products **2a–e** were fully established by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR and UV–vis spectral data. It should be noted that the very low solubility of **2c** precluded its ^{13}C NMR measurement. The ESI mass spectra of **2a–e** showed the correct molecular ion peaks. The ^{1}H NMR spectra of **2a–e** displayed a broad singlet at 10.54–11.33 ppm for the =NH group. In the ^{13}C NMR spectra of **2a**, **2b**, **2d** and **2e**, the imine carbon and the two sp^3-carbons of the C_{60} cage appeared at 173.12–178.52 ppm, 76.60–79.91 ppm and 69.74–71.94 ppm, respectively. More than forty-nine peaks for **2a**, **2b** and **2d** and twenty-nine peaks for **2e** were observed in the range 153.46–132.01 ppm, consistent with the C_1 (**2a**, **2b** and **2d**) and C_s (**2e**) symmetry of their molecular structures. The IR spectra of **2a–e** showed absorptions at 3272–3278 cm^{-1} and 1622–1626 cm^{-1} due to the C=NH group. The UV–vis spectra of **2a–e** exhibited a peak at 428–429 nm, which is a diagnostic absorption for a cycloadduct of C_{60} at the [6,6]-junction.

Products **3a**, **3b** and **3d** are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature.[8a] Product **3c** was fully characterized by its MS, ^{1}H NMR, ^{13}C NMR, FT-IR and UV–vis spectral data. The MS (+ESI) of **3c** showed its molecular ion peak at *m/z* 872. Its ^{1}H NMR spectrum exhibited a singlet at 5.54 ppm for the methine proton and two doublets at 8.37 and 7.62 ppm for the aromatic protons. In the ^{13}C NMR spectrum of **3c**, the peaks at 187.49 and 43.75 ppm were assigned to the carbonyl carbon and methine carbon, the two sp^3-carbons of the C_{60} cage appeared at 71.89 ppm, and twenty-eight peaks including overlapped ones were observed in the range 147.57–129.52 ppm due to the fifty-eight sp^2-carbons of the C_{60} skeleton and six aromatic carbons, consistent with the C_s symmetry of its molecular structure.

Just as the C=S bond of the thioamide moiety in our previously synthesized fullerene derivative was moisture sensitive,[18] the C=N bond of the thioimidate unit in products **2a–e** was prone to

hydrolysis. C_{60}-fused 2-iminotetrahydrothiophene derivatives **2a–e** could be converted to C_{60}-fused 2-oxotetrahydrothiophene derivatives **4a–e** in excellent yields in a mixture of CS_2–THF–H_2O in the presence of *p*-toluenesulfonic acid (PTSA) at room temperature (Scheme 3). The isolated yields for products **4a**, **4b**, **4c**, **4d** and **4e** were 98%, 95%, 96%, 92% and 93%, respectively.

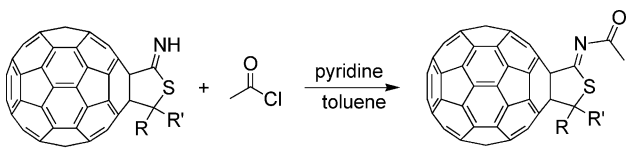


2a-e **4a-e**

2a, **4a**: R = H, R' = 4 -CH_3OPhCO; **2b**, **4b**: R = H, R' = PhCO;
2c, **4c**: R = H, R' =4 -ClPhCO; **2d**, **4d**: R = H, R' = $CO_2C(CH_3)_3$
2e, **4e**: R = R' = $CO_2C_2H_5$

Scheme 3

To demonstrate the utilization of 2-iminotetrahydrothiophene derivatives **2a–e**, the acetylation of the imine group was successfully exploited to generate C_{60}-fused 2-acetamidotetrahydrothiophene derivatives **5a–e** by the reaction of **2a–e** with acetyl chloride in the presence of pyridine (Scheme 4). The isolated yields for products **5a**, **5b**, **5c**, **5d** and **5e** were 94%, 95%, 95%, 92% and 92%, respectively.



2a-e **5a-e**

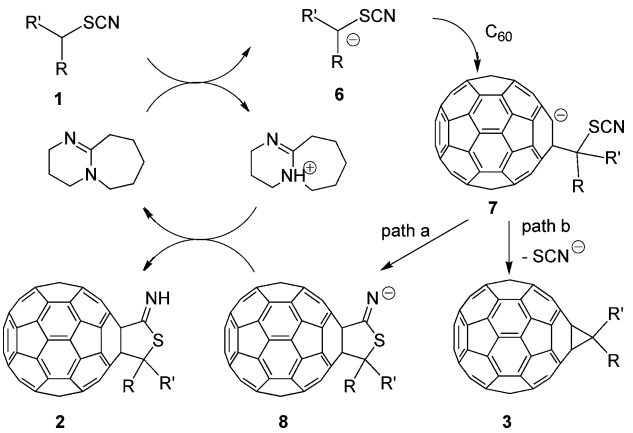
2a, **5a**: R = H, R' = 4 -CH_3OPhCO; **2b**, **5b**: R = H, R' = PhCO;
2c, **5c**: R = H, R' =4 -ClPhCO; **2d**, **5d**: R = H, R' = $CO_2C(CH_3)_3$
2e, **5e**: R = R' = $CO_2C_2H_5$

Scheme 4

The solubility of the resulting hydrolyzed products **4a–e** and *N*-acetylated products **5a–e** in CS_2 and $CDCl_3$ was improved dramatically over that of adducts **2a–e**, facilitating their NMR measurements.

Compounds **4a–e** and **5a–e** were also fully characterized by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR and UV–vis spectral data. Compared with compounds **2a–e**, products **4a–e** and **5a–e** lacked the absorptions at 3272–3278 cm^{-1} in their IR spectra and the broad singlet in their ^{1}H NMR spectra for the =NH group. A new peak at 2.52–2.55 ppm for the methyl group was observed in the ^{1}H NMR spectra of **5a–e**. In the ^{13}C NMR spectra of **4a–e**, the carbonyl carbon derived from the hydrolysis of the C=NH group appeared at 191.72–194.60 ppm. In the ^{13}C NMR spectra of **5a–e**, besides the corresponding peaks of **2a–e**, new peaks were found at 182.09–185.00 ppm and 24.80–25.95 ppm due to the acetyl group. It is interesting to note that the chemical shift difference of the two sp^3-carbons of the C_{60} cage in compounds **4a–e** (67.14–69.77 and 79.53–83.27 ppm) and **5a–e** (68.65–71.04 and 79.01–82.31 ppm) increased to 11.72–13.50 ppm and 10.06–11.27 ppm, respectively, from 6.64–8.08 ppm for products **2a–e**, due to the downfield shift of the low-field sp^3-carbon and the upfield shift of the high-field sp^3-carbon of the C_{60} skeleton.

A possible reaction mechanism for the formation of products **2a–e** and **3a–d** is shown in Scheme 5. The deprotonation of thiocyanate **1** by DBU generates carbanion **6**, which attacks C_{60} to yield intermediate **7**. The resulting fullerenyl anion **7** could go through two pathways: in path a, the fullerenyl carbanion attacks the C≡N bond of the SCN group to afford the five-membered heterocyclic anion **8**, which is then protonated to give the final product **2**; in path b, intramolecular nucleophilic addition of the fullerenyl carbanion to the carbon connected with the SCN group affords the Bingel-type adduct **3**, accompanied by extrusion of the SCN^- anion.



Scheme 5

Conclusions

A novel procedure for the synthesis of tetrahydrothiophene-fused fullerene derivatives through nucleophilic cycloaddition of thiocyanates with C_{60} has been established for the first time. The current protocol provides easy access to tetrahydrothiophene-fused fullerene derivatives that may be of biological importance, and are difficult to synthesize by other methods.

Experimental

Procedure for the synthesis of compounds 2a–e and 3a–d by the reaction of C_{60} with thiocyanates 1a–e

A mixture of C_{60} (36.0 mg, 0.05 mmol), thiocyanate **1a** (**1b**, **1c**, **1d**, or **1e**) and DBU in the desired amounts was dissolved in toluene (25 mL) and stirred at room temperature. The reaction was monitored by TLC and stopped at the designated time. After evaporation of the toluene, the residue was separated on a silica gel column with CS_2, then CS_2–ethyl acetate as the eluent, to give unreacted C_{60}, product **2a** (**2b**, **2c**, **2d**, or **2e**) and product **3a**[8a] (**3b**[8a], **3c**, or **3d**[8a]), respectively. The yields, along with the recovered C_{60}, are listed in Table 2.

Preparation of compounds 4a–e by the hydrolysis of compounds 2a-e

Compound **2a** (or **2b–e**, 0.02 mmol) was added to a mixture of CS_2–THF–H_2O (15 mL, 10 : 1 : 0.1) and *p*-toluenesulfonic acid

(0.04 mmol) and the reaction mixture was vigorously stirred at room temperature for 12 h. After evaporation of the solvent, the residue was separated on a silica gel column with CS–ethyl acetate as the eluent to give product **4a** (or **4b–e**).

Preparation of compounds 5a–e by the acetylation of compounds 2a–e

A mixture of **2a** (or **2b–e**, 0.02 mmol) and pyridine (0.08 mmol) was dissolved in CS_2 (15 mL), then to the solution was added acetyl chloride (0.08 mmol) and the reaction was stirred at room temperature for 1 h. After evaporation of excess CS_2, the residue was separated on a silica gel column with CS_2–ethyl acetate as the eluent to give product **5a** (or **5b–e**).

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Notes and references

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