



Base-promoted reaction of C₆₀Cl₆ with thioamides: an access to [60] fullereno[1,9-*d*] thiazoles



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ABSTRACT

Regioselective reaction of C₆₀Cl₆ with thioamides via a radical annulation to form fullereno thiazole derivatives is reported. The reaction is promoted by K₂CO₃, which might deprotonate thioamide to initiate a single electron transfer from thioamide anion to C₆₀Cl₆. The experiments with various thioamides establish the proposed base-promoted reaction as a facile route for synthesis of fullereno fused thiazole derivatives starting from C₆₀Cl₆, a prevalent synthon in fullerene chemistry. In addition, the tunable electrochemical properties of the fullereno thiazole products have been investigated for their potential photovoltaic application.

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1. Introduction

Fullerene derivatives have attracted considerable attention due to their potential applications in the fields such as photovoltaic and biological materials.¹ Various derivatization methods have been developed to modify the fullerene cage over the years. Among them, hexachlorofullerene C₆₀Cl₆ is a prevalent synthon for preparation of novel fullerene derivatives by substitution of chlorine atoms with appropriate organic groups.² For example, Troshin et al.³ reported a highly water-soluble fullerene derivative through Arbuzov-type reaction of C₆₀Cl₆ with trialkyl phosphites. Darwish and co-workers⁴ treated C₆₀Cl₆ with phenol to give corresponding benzo[*b*]furano fullerenes. Stable pentacyanofullerene anion [C₆₀(CN)₅][−] was obtained by reaction of C₆₀Cl₆ with organic cyanide.⁵ Recently, our group succeeded in converting C₆₀Cl₆ into fullerocyclobutene derivatives through a copper(I)-mediated radical annulation reaction.⁶ Herein we report another unexpected regioselective reaction involving C₆₀Cl₆ and thioamide in the presence of K₂CO₃. Promoted by K₂CO₃ base, two out of six chlorine atoms on fullerene skeleton are replaced by thiazole regioselectively, and the other four chlorine atoms leave from the fullerene cage to result in fullerene-fused thiazole compound. The

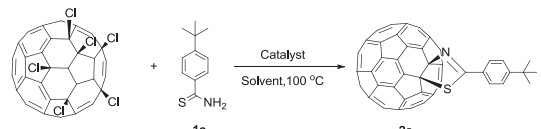
mechanism responsible for the reaction is different from those previously reported by Itami and co-workers⁷ for synthesis of fullerene-fused thiazole derivatives using aziridinofullerene as precursor. The present regioselective reactions starting from the prevalent C₆₀Cl₆ (with quantitative yield) is efficient over Itami's method using aziridinofullerene (with ~43% yield) as reactant, and is different from the fullerene-fused oxazole derivatization with the heteroatom involved.⁸

2. Results and discussion

4-*tert*-Butylthiobenzamide (**1a**) was used as a model substrate for optimizing the reaction conditions, including bases, phase transfer catalysts (PTCs), and solvent systems. Only a trace amount of product **2a** was obtained without base added (Table 1, entry 1). The reaction was improved in the presence of K₂CO₃, but the isolated yield of **2a** (<10%) was unsatisfactory (Table 1, entry 2). The effect of solvent was also critical to the catalytic reaction. With a mixture of *o*-DCB (5 mL) and toluene (50 mL) as solvent media, product **2a** was obtained in 15% yield (Table 1, entry 3), which was significantly improved by applying tetrabutylammonium hydrogen sulfate (TBAHS) as phase transfer catalyst (Table 1, entry 4). Using Na₂CO₃ as the base in replacement of K₂CO₃ reduced the yield to 9% (Table 1, entry 5). Stronger base such as Cs₂CO₃ resulted in dechlorination of reactant C₆₀Cl₆ leading to lower yield under otherwise the same reaction conditions. Replacing TBAHS with

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Table 1
Reaction of C₆₀Cl₆ with **1a** under selected conditions^a



Entry	Base	PTC ^b	Solvent (mL) ^c	Yield (%) ^d
1	None	None	PhCH ₃	Trace
2	K ₂ CO ₃	None	PhCH ₃	<10%
3	K ₂ CO ₃	None	<i>o</i> -DCB/PhCH ₃ (5:50)	15
4	K₂CO₃	TBAHS	<i>o</i>-DCB/PhCH₃(5:50)	32
5	K ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCl(5:50)	20
6	Na ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCH ₃ (5:50)	9
7	K ₂ CO ₃	PEG600	<i>o</i> -DCB/PhCH ₃ (5:50)	16
8	K ₂ CO ₃	TOMAB	<i>o</i> -DCB/PhCH ₃ (5:50)	13
9 ^e	K ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCH ₃ (5:50)	28
10 ^f	K ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCH ₃ (5:50)	20
11 ^f	K ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCH ₃ (5:50)	25
12 ^g	K ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCH ₃ (5:50)	23
13 ^h	K ₂ CO ₃	TBAHS	<i>o</i> -DCB/PhCH ₃ (5:50)	0

The bold values represent the optimal reaction conditions.

^a All reactions were performed with 0.05 mmol of C₆₀Cl₆, 0.10 mmol of **1a**, 0.50 mmol of base and 0.005 mmol of PTC in the indicated solvent at 100 °C for 12 h unless otherwise noted.

^b PTC=phase transfer catalyst, TBAHS=tetrabutylammonium hydrogen sulfate, PEG600=polyethylene glycol 600, TOMAB=trioctyl methyl ammonium bromide.

^c *o*-DCB=*o*-dichlorobenzene.

^d Isolated yield.

^e 20 equiv of K₂CO₃.

^f The experiments were carried out at a temperature of 80 or 120 °C.

^g The reaction time was 24 h.

^h The experiment was carried out starting from C₆₀ and **1a**.

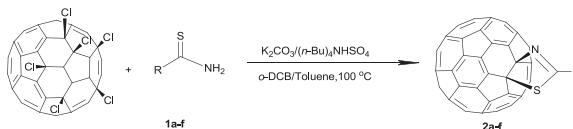
polyethylene glycol 600 or trioctyl methyl ammonium bromide under otherwise the same conditions resulted in a decrease in the yield too (Table 1, entries 7–8). It is noteworthy that increasing the loading of K₂CO₃ from 10 to 20 equiv leads a negative result (Table 1, entry 4 vs entry 9). Neither the reaction temperature nor the reaction time showed serious influence on the reaction (Table 1, entries 10–12). Accordingly, the optimal reaction conditions were selected with 2 equiv **1a**, 10 equiv K₂CO₃, and 0.1 equiv TBAHS (Table 1, entry 4). It should be noted that reaction of **1a** with C₆₀ failed to give the expected product under the same reaction condition (Table 1, entry 13). Both ¹H and ¹³C NMR spectra of **2a** match well with the identified structures [see Supplementary data (SD)].

Reactions of C₆₀Cl₆ with other thioamides under the optimized reaction conditions (as described above) were carried out. As shown in Table 2, substrates **1a–f** bridged with aromatic or non-aromatic groups afforded the desired products **2a–f** in 23–42% yields. In principle, the aromatic thioamides linked with electron-donating groups are of higher reactivity. The reactions involving the aromatic thioamides having electron-donating groups thus afford higher yields than those containing electron-withdrawing groups (Table 2, entries 1–3). The reaction of nonaromatic thioamide **1d** gives a relatively high yield of 42% (Table 2, entry 4). While heterocyclic thioamides **1e** and **1f** participated in the reaction to afford **2e** and **2f** in 28 and 23% yield, respectively (Table 2, entries 5–6).

New compounds **2b–f** were characterized by ¹H NMR, ¹³C NMR, IR, and UV–Vis spectral data. All of the mass spectra of these fullerene products gave matchable molecular ion peaks. In addition, geometrical structure of product **2f** was further identified by X-ray diffraction analysis (see the SD).⁹ In agreement with NMR spectra data, as shown in Fig. 1, the thiazole was regioselectively fused onto the [6,6] bond of the fullerene cage.

A possible mechanism for the reaction is shown in Scheme 1, which is proposed according to the present experimental evidence and literature.^{6,10} Considering electron absence in both C₆₀ cage and chlorine atom, single electron transfer (SET) from thioamide anion

Table 2
Reaction of C₆₀Cl₆ with **1a–f** under optimized conditions^a



Entry	R	2	Yield (%) ^b	Recovered C ₆₀ (%)
1	(H ₃ C) ₂ -C ₆ H ₄	2a	32	52
2	H ₃ C(H ₂ C) ₂ OOC-	2b	25	65
3	H ₃ C(H ₂ C) ₂ O-	2c	35	48
4	(CH ₂) ₃ COOC ₂ H ₅	2d	42	45
5	(CH ₂) ₄ CH ₃	2e	28	62
6	H ₃ C(H ₂ C) ₄ -S-	2f	23	58

^a All reactions were performed with 0.05 mmol of C₆₀Cl₆, 0.10 mmol of **1**, 0.5 mmol of K₂CO₃ and 0.005 mmol of TBAHS in *o*-DCB (5 mL)/PhCH₃ (50 mL) at 100 °C for 24 h.

^b Isolated yield.

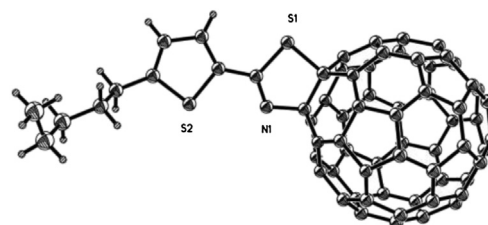
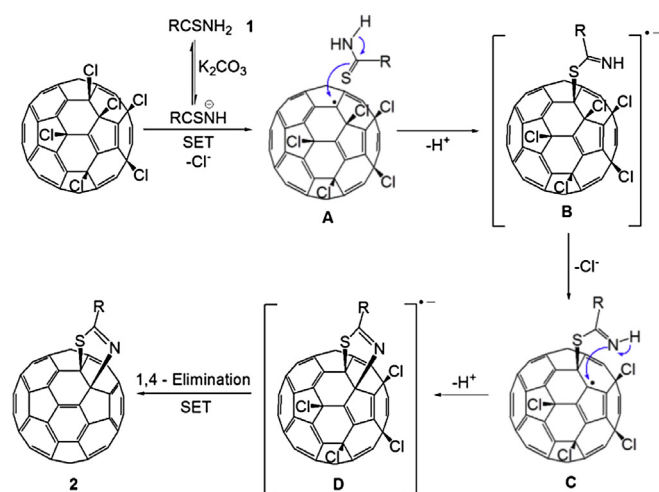


Fig. 1. Crystallographic structure of **2f**.



Scheme 1. Proposed mechanism for the formation of [60]fullereno[1,9-d]thiazole derivatives **2** (SET = single electron transfer).

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