Tetrahedron Letters 58 (2017) 2566–2570

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Lewis base-catalyzed double nucleophilic substitution reaction of *N*-tosylaziridinofullerene with thioureas or guanidines

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ARTICLE INFO

Article history:
Received 30 March 2017
Revised 13 May 2017
Accepted 15 May 2017
Available online 17 May 2017

Keywords:
Tosylaziridinofullerene
Double nucleophilic substitution
Thiourea
Guanidine

ABSTRACT

Lewis base-catalyzed double nucleophilic substitution reaction of *N*-tosylaziridinofullerene with thioureas or guanidines affords the fullerothiazolidin-2-imine or fulleroimidazolidin-2-imine derivatives, respectively. In the case of unsymmetrical thioureas connecting an alkyl and an aryl group on each of the nitrogen atom, the transformation exhibits excellent chemoselectivity with only the aryl substituted nitrogen atom bonding to C_{60}. The generated tri-4-methoxyphenyl substituted fulleroimidazolidin-2-imine reacts with CS_2 smoothly to generate di-4-methoxyphenyl fulleroimidazolidin-2-thione.

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Introduction

There has been a good understanding of the chemical reactivity of C_{60} and a large number of highly functionalized fullerenes have been efficiently synthesized by various techniques.[1] Nevertheless, the diversity in the structures of fullerene derivatives may lead to the creation of new application in the fields of material and biomedicine science,[2] further exploration and development of new synthetic methods toward organofullerenes with sophisticated and unprecedented architectures is still required.[3] At present, most of the fullerene derivatives are prepared directly from pristine C_{60} through one-step reaction. However, not all the fullerene derivatives can be easily synthesized from C_{60}. Thus, the development of new routes to access functionalized fullerenes with novel structure from an easily prepared fullerene derivative is in demand. For instance, the fullerene epoxide,[4] *N*-tosylaziridinofullerene,[5] azafulleroids,[6] and NFSI adduct of C_{60}[7] have been reported to undergo various transformations to furnish a diversity of functionalized fullerenes. Especially the *N*-tosylaziridinofullerene, which can be easily synthesized from sulfonamides in good yield,[8] not only takes place a formal [3 + 2] reaction with isocyanates, CO_2,[9] or carbonyl compounds[10] with the reserve of “TsN” unit but also undergo a unique double nucleophilic substitution reaction with dinucleophiles accompanied by the loss of “TsN” unit.[11] The CF_3SO_3H and combination of $HPCy_3BF_4$-NaH have proved to be the effective catalysts.[5b,9] Recently, we applied commonly used bases such as DMAP (4-dimethylaminopyridine) or NMI (*N*-methylimidazole) as a catalyst in the double nucleophilic substitution of *N*-tosylaziridinofullerene with amidines or ureas for the easy preparation of cyclic 1,2-diaminated [60] fullerenes.[11a,11b] The easy operation process and the highly synthetic efficiency encouraged us to develop more transformation through the easily available *N*-tosylaziridinofullerene. Thiourea and guanidine have structure similarity with urea just with the variation of C=O double bonds to C = S/N double bonds (Fig. 1). We were inquisitive about whether the thiourea and guanidine can react with *N*-tosylaziridinofullerene to afford two new classes of organofullerenes *via* a similar transformation.

Results and discussion

Our investigation began with the reaction of *N*-tosylaziridinofullerene **1** with 1,3-dibenzylthiourea **2a**. Those reported effective catalyst in the transformations of *N*-tosylaziridinofullerene such as CF_3SO_3H, $BF_3{\cdot}Et_2O$, DMAP, and NMI were tried firstly (Table 1, entries 1–4).[5b,10,11a,11b] The CF_3SO_3H and BF_3 Et_2O showed no catalytic activity and almost all of the **1** was converted to C_{60} (Table 1, entries 1 and 2). Using DMAP as the catalyst gave a single product. However, the NMR analysis revealed that it was not the anticipated diaminated product but the fullerothiazolidin-2-imine **3a**. The yield was not satisfactory and only 51% yield of **3a** was obtained after stirring for 3 h at 80 °C

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http://dx.doi.org/10.1016/j.tetlet.2017.05.048

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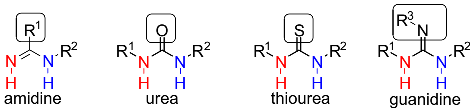
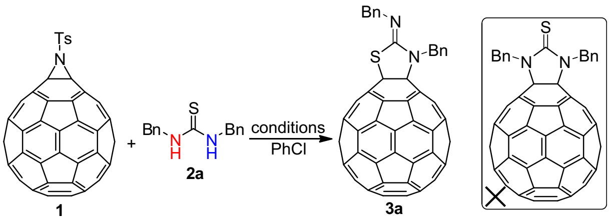


Fig. 1. Structures of the amidine, urea, thiourea, and guanidine.

(Table 1, entry 3). Increasing the temperature to 120 °C had no improvement on the yield because a large amount of *N*-tosylaziridinofullerene was transformed to C_{60}. Although increasing the amount of DMAP to 1 equiv could complete the conversion within 1 h and gave higher yield of **3a**, large decomposition of **1** to C_{60} was inevitable (Table 1, entry 4). The NMI gave a decent yield of **3a**, however, a considerable decomposition of **1** to C_{60} occurred also (Table 1, entry 5). Next, other Lewis base/acid catalysts such as Sc(OTf)$_3$, Zn(OTf)$_2$, Cu(OTf)$_2$, Et_3N, pyridine, and DABCO were examined (Table 1, entries 6–13). To our delight, the DABCO could efficiently catalyze the reaction, affording 91% yield of the product within 1 h at 80 °C (Table 1, entry 8). Reducing the amount of DABCO to 0.2 equiv led to longer reaction time to complete the reaction, whereas, more starting material was decomposed to C_{60} (Table 1, entry 9). Replacing DABCO with Et_3N, pyridine, or K_2CO_3 resulted in dramatic decrease in the yield or no reaction (Table 1, entries 6, 7, and 10). The commonly used Lewis acids such as Sc(OTf)$_3$, Zn(OTf)$_2$, and Cu(OTf)$_2$ also displayed certain catalytic activity, albeit with a much lower yield (Table 1, entries 11–13).

With the optimal conditions in hand, the substrate scope for the transformation was evaluated. As illustrated in Table 2, the preparative scope was rather general regardless of whether alky or aryl groups were presented on the nitrogen atoms, giving moderate to excellent yield of fullerothiazolidin-2-imines **3**. For dialkylated thioureas, a noticeable steric effect was observed. Compared with the high yield of **3a** and **3b**, only 69% yield of **3c** was obtained for the *N*,*N*′-diisopropylthiourea **2c** and no desired product was isolated for *N*,*N*′-di-tert-butylthiourea. When one of the tert-butyl was replaced by benzyl, the reaction occurred to selectively provide **3d** in 88% yield with sterically less hindered nitrogen atom bonding to C_{60}. In terms of the diarylated thioureas, using DABCO as the catalyst gave a low conversion as detected by TLC. Replacing DABCO with DMAP and increasing the temperature to 120 °C gave good yield of **3f–i**. It should be noted that only catalytic amount of DMAP was required. For the unsymmetrical diarylated thiourea **2j**, which connected an electron-donating and electron-withdrawing group on each of the nitrogen atom, its reaction with **1** showed low chemoselectivity, affording an inseparable mixture of the two isomers **3j** and **3j**′ (**3j**:**3j**′ = 1.44:1) in overall 69% yield. In the major isomer, the nitrogen atom bearing an electron-rich aryl group bonded to C_{60} probably due to its stronger nucleophilicity. To investigate the influence of different types of substituents on the reaction, the thioureas **2k–m** having an alkyl and an aryl group on each of the nitrogen atom were prepared and introduced to the reaction. When one of the nitrogen atoms linked with an alkyl group, DABCO could effectively catalyze the transformation. It was noteworthy that the reaction of **1** with **2k–m** showed excellent chemoselectivity and only single isomer was obtained with the arylated nitrogen atom bonging to C_{60}. In the case of the *N*-benzyl-*N*′-tosylthiourea **2n**, although it displayed lower reactivity, its reaction with **1** showed high selectivity and furnished single isomer **3n**. The catalytic system showed a high degree of functional group tolerance and the alkenyl, ester, hydroxyl, and acetal groups were compatible with the conditions to afford good yields of **3e**, **3i**, **3j**, **3l**, and **3m**. Compared with our previous reported Lewis base-catalyzed reaction of **1** with amidines or ureas, in which the two substituents of amidines were restricted to both aryl groups and one of the substituent of ureas was limited to electron withdrawing group such as Ts and Bz group,[11a,11b] the thioureas displayed more extensive substrate scope in its reaction with **1**.

Table 1
Screening of the Catalysts.[a]



Entry	Conditions	Molar ratio[b]	T (°C)	Time (h)	Yield (%)[c]
1	$BF_3{\cdot}Et_2O$	1:1.5:5	80	0.5	0
2	CF_3SO_3H	1:1.5:2	80	0.5	0
3	DMAP	1:1.5:0.2	80	3	51
4	DMAP	1:1.5:1	80	1	67
5	NMI	1:1.5:1	80	2	71
6	Et_3N	1:1.5:1	80	6	40
7	pyridine	1:1.5:1	80	6	35
8	**DABCO**	**1:1.5:1**	**80**	**1**	**91**
9	DABCO	1:1.5:0.2	80	4	77
10	K_2CO_3	1:1.5:2	120	3	0
11	Sc(OTf)$_3$	1:1.5:0.5	120	4	53
12	Zn(OT f)$_2$	1:1.5:0.5	120	6	21
13	Cu(OTf)$_2$	1:1.5:0.5	120	4	47

[a] Unless notified, the reactions were carried out (**1**, 0.02 mmol) in 2.5 mL of dry chlorobenzene.

[b] **1**:**2a**:catalyst.

[c] Isolated yield.

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