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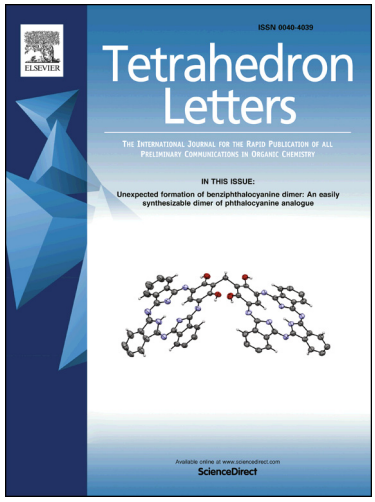

Lewis Base-Catalyzed Double Nucleophilic Substitution Reaction of *N*-Tosylaziridinofullerene with Thioureas or Guanidines

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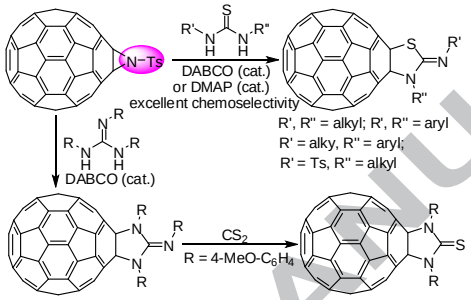

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ABSTRACT

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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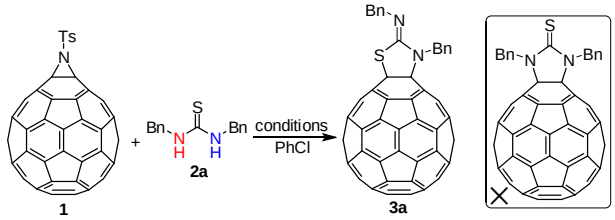
Table 1 Screening of the Catalysts[a]



entry	conditions	molar ratio[b]	T (ºC)	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.

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 an 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,b] 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 (Figure 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.

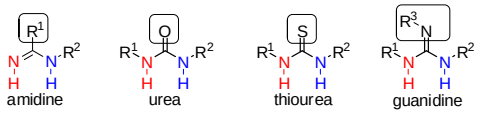
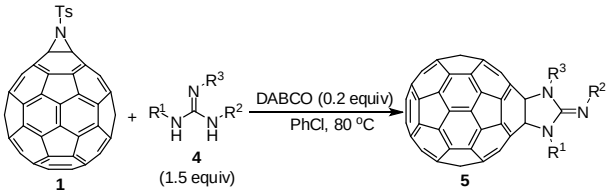


Figure 1 Structures of the amidine, urea, thiourea, and guanidine

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 $BF_3{\cdot}Et_2O$ 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 ºC (Table 1, entry 3). Increasing the temperature to 120 ºC 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 ºC (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).

Table 3 DABCO-Catalyzed Reaction of Aziridinofullerene **1** with Guanidines



entry	substrate	product
1	**4a** (R^1, R^2, R^3 = 4-MeC_6H_4)	**5a** (1 h, 85%)
2	**4b** (R^1, R^2, R^3 = 4-$MeOC_6H_4$)	**5b** (1 h, 67%)
3	**4c** (R^1, R^2, R^3 = 4-ClC_6H_4)	**5b** (2.5 h, 78%)
4	**4d** (R^1, R^2 = 4-MeC_6H_4, R^3 = n-Bu)	very low yield, two isomers
5	**4e** (R^1, R^2, R^3 = Bn)	**5d** (0.5 h, 0%)

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

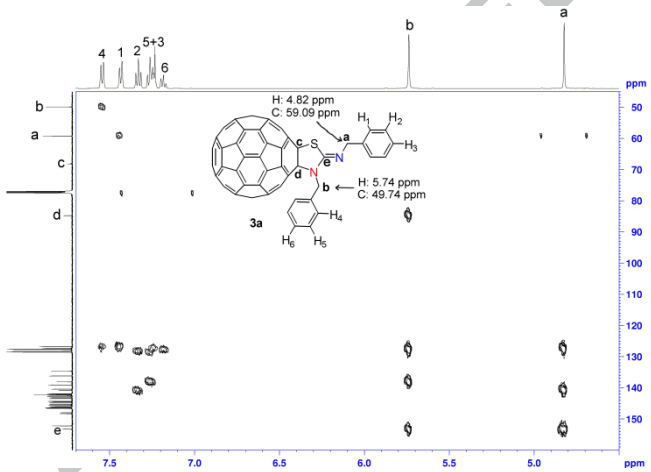
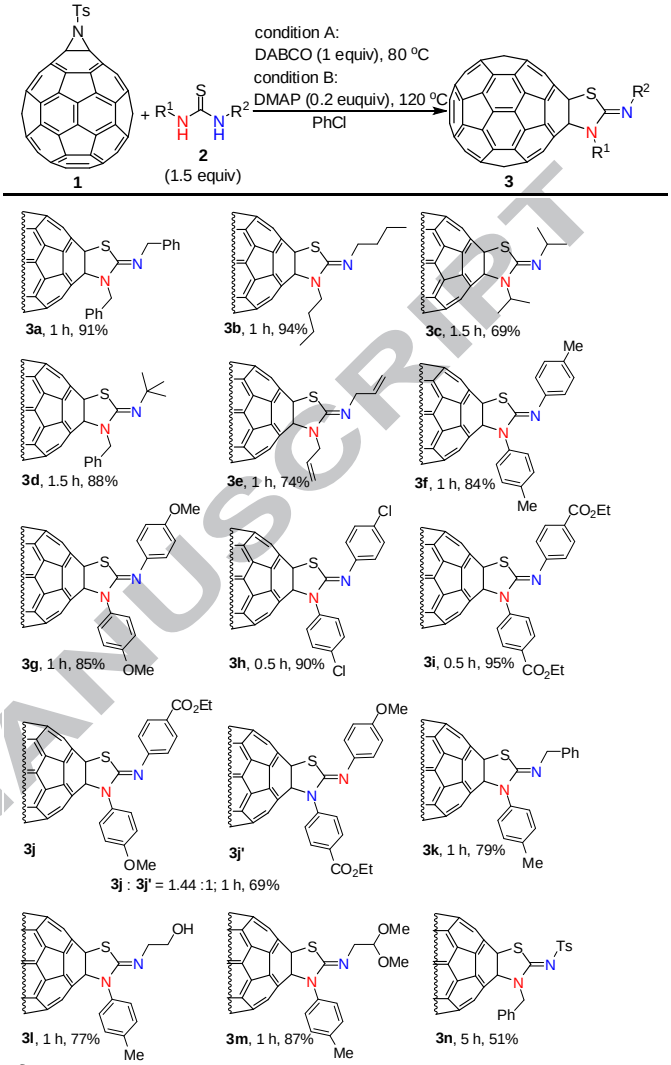


Figure 2 HMBC Spectrum of **3a** in $CS_2/CDCl_3$ (500 MHz)

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 chemoselctivity, 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

Table 2 Substrate Scope



[a] The condition A was applied for **3a-d** and **3k-n**. The condition B was applied for **3f-j**.

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,b] the thioureas displayed more extensive substrate scope in its reaction with **1**.

Encouraged by the promising results achieved above, we next turned our attention to investigate the preparation of fulleroimidazolidin-2-imines through a similar method. We were pleased to find that the DABCO-catalyzed reaction of *N*-tosylaziridinofullerene **1** with 1,2,3-tri-*p*-tolylguanidine **4a** afforded the desired fulleroimidazolidin-2-imine **5a** in 85% yield. Either electron-donating or electron-withdrawing group on the phenyl had no influence on the reaction. When one of the aryl groups was replaced by an alkyl group, the reaction proceeded miserably and afforded very low yield of product as inseparable mixture of two isomers. Meanwhile, large amount of *N*-tosylaziridinofullerene **1** decomposed to C_{60}. Trialkylguanidine was not suitable for this transformation yet and all of the staring material **1** decomposed. A possible explanation might be due to the strong basicity of alklylated guanidines because in our previous work we found that the strong organic base such as DBU could not catalyze the reaction of **1** with amidines and all of the **1** was transformed to C_{60} and unidentified product with very high polarity.[11b]

During the course of NMR analysis of product **5b** with CS_2-$CDCl_3$ as the solvent, the compound **5b** was found reacting with CS_2 slowly to furnish a single product with lower polarity. Stirring a solution of **5b** in CS_2-$CHCl_3$ at room temperature for 5 days afforded the fulleroimidazolidinthione **6** in 78% yield. In comparison, the **5a** and **5c** was much more stable in carbon disulfide.

The structures of fullerothiazolidin-2-imines **3** and fulleroimidazolidin-2-imines **5** were unambiguously characterized by their MALDI-TOF HRMS, ^{1}H NMR, ^{13}C NMR, and UV−vis spectra (Supporting Information). In the ^{1}H NMR and ^{13}C NMR spectra of **3a**, a noticeable difference between the two CH_2 groups was observed. The two peaks at 84.60 and 68.03 ppm was attributed to the two sp^3-carbons of C_{60} linking to nitrogen and sulfur atom, respectively. The higher electronegativity of nitrogen atom than sulfur atom resulted in the downfield shift. To accurately assign the two CH_2 groups, **3a** was further taken the H-H COSY and HMBC spectroscopic analysis (Figure 2 and Supporting Information), which would be helpful to confirm the structure of **3d**, **3j**, **3k**, **3l**, **3m**, and **3n** generated from the unsymmetrical thioureas. The observed ^{3}J C_b-H_d and ^{1}J C_a-H_a correlation precisely discriminated the two CH_2 groups (Figure 2). The CH_2 group (**b**) attached on the saturated nitrogen atom showed downfield ^{1}H NMR shift (5.74 *vs* 4.82 ppm) and upfield ^{13}C NMR shift (49.74 *vs* 59.09 ppm) compared with the CH_2 group (**a**) attaching on the imine nitrogen atom. From the ^{3}J C_b-H_4 and ^{3}J C_a-H_1 correlation and the H-H COSY spectrum the signals for the two phenyl ring could be assigned accurately. By comparison of the ^{1}H NMR and ^{13}C NMR chemical shifts of the methylene group in compounds **3d** (5.63 and 49.83 ppm), **3n** (5.75 and 51.06 ppm), and **3k** (4.76, 59.57 ppm) with that of **3a** we could precisely infer their structure (Figure 3). In the ^{1}H NMR spectrum of **5a**, the 4-

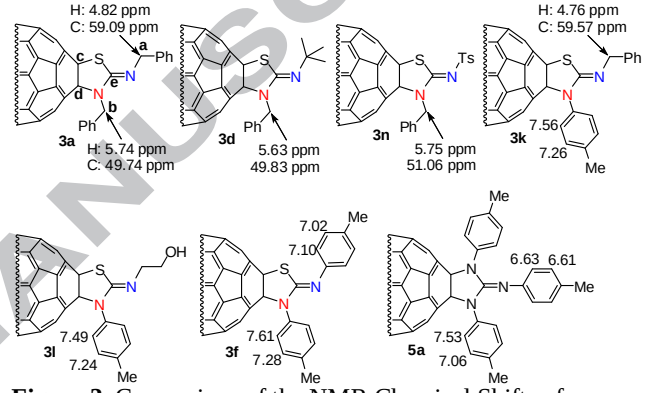
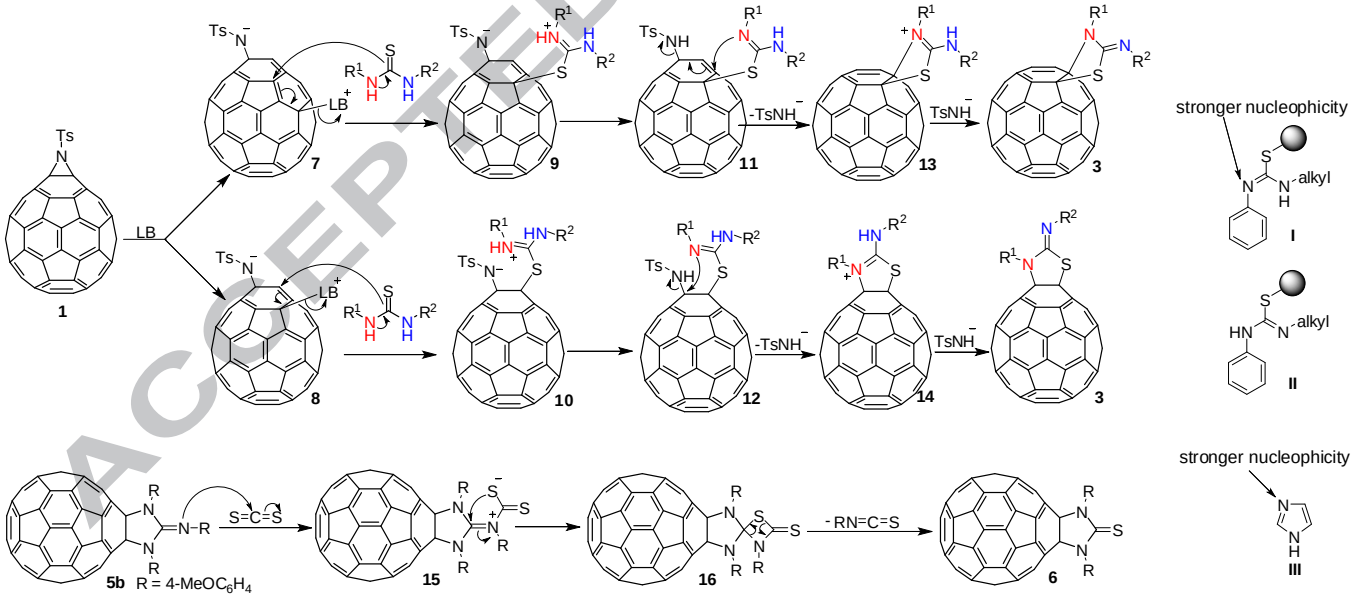
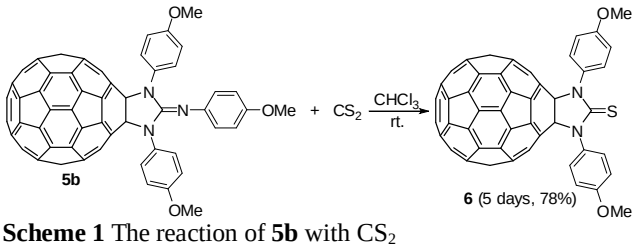


Figure 3 Comparison of the NMR Chemical Shifts of Compounds **3a**, **3d**, **3n**, **3k**, **3l**, **3f**, and **5a**



Scheme 2 Proposed Mechanism



Scheme 1 The reaction of **5b** with CS_2

methylphenyl group attached on the saturated nitrogen atom clearly showed more downfield shift than that of attached on the imine nitrogen atom. According to this, in the ^{1}H NMR spectrum of **3f**, the two doublets with downfield shift (7.28 and 7.61 ppm) was assigned to the aryl ring attached on the saturated nitrogen atom, whereas the two doublets with upfield shift (7.02 and 7.10 ppm) was attributed to the aryl ring attached on the imine nitrogen atom (Figure 3). The observed difference of the two aryl ring further supported the structure assignment of **3k**, **3l**, and **3m**, in which the chemical shift of 7.49-7.56 and 7.22-7.26 ppm for the 4-methyphenyl ring implied it attached on the saturated nitrogen atom (Figure 2).

A plausible mechanism for the formation of **3**, **5**, and **6** was depicted in Scheme 2. Nucleophilic attack of the Lewis base on the fullerene cage of **1** along with the ring-opening of azirdine ring would generate the zwitterion **7** or **8**,[9] which undergoes further S_N2' reaction with thiourea to give **9** or **10**. After intramolecular proton exchange, further S_N2' reaction affords **13** or **14** and the subsequent deprotonation furnishs the fullerothiazolidin-2-imine **3**. No diaminated product is generated probably due to the stronger nucleophilicity of sulfur atom than that of nitrogen atom. For the unsymmetrical thiourea bearing an alkyl and an aryl group on each of the nitrogen atom, the intermediate **11** (**12**) preferred the structure of **I** but not **II** because in the reported *S*-alky isothioureas the aryl group connected on the imine nitrogen atom.[12] Like the imidazole (**III**), the imine nitrogen should show stronger nucleophilicity than the saturated nitrogen atom linking with alky group, which results in the excellent chemoselectivity. At present, we have no a definite answer to the relationship between the base choice and the substituent on the nitrogen atom. The reaction of **1** with guanidine takes the same process to afford fulleroimidazolidin-2-imine **5**. When the nitrogen atom linked with a 4-methoxyphenyl group, the strong electron donating character of the methoxyl group increases the nucleophilicity of the nitrogen atom dramatically. Nucleophilic addition of **5b** with CS_2 followed by an intramolecular nucleophilic cyclization generates an intermediate **16**, which dissociates to give product **6** and 4-methoxyphenylisothiocyanate. The less electron-donating character of chloro and methyl group than methoxyl group results in the low nucleophilicity of imine-nitrogen atom in **5a** and **5c**, which explains the stability of **5a** and **5c** in CS_2 compared with **5b**. The compounds **3g** and **3j'** are very stable in CS_2. It can be explained that the imine nitrogen atom of *S*-substituted isothiourea has weaker basicity and nucleophilicity than that of guanidine because the electron-donating conjugation effect of nitrogen atom is stronger than sulfur atom.

Conclusions

In summary, an easy preparation of two new classes of fullerothiazolidin-2-imine or fulleroimidazolidin-2-imine derivatives *via* Lewis base-catalyzed double nucleophilic reaction of *N*-tosylaziridinofullerene with thioureas or guanidines has been developed. The reaction of *N*-tosylaziridinofullerene with unsymmetrical thioureas bearing an alkyl and an aryl group on each of the nitrogen atom shows excellent chemoselectivity. The tri-4-methoxyphenyl substituted fulleroimidazolidin-2-imine reacts with CS_2 smoothly to generate fulleroimidazolidin-2-thione.

Acknowledgments

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Supplementary Material

General synthetic procedures, characteristic data, and NMR spectra of the products can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.

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12. It could be clearly seen from the ^{1}H NMR sepectrum the hydrogen on nitrogen atom was split by the adjacent alkyl group. For example, see: Mampuys, P.; Zhu, Y.; Vlaar, T.; Ruijter, E.; Orru, R. V. A.; Maes, B.

Highlight

1. Base catalyzed reaction of *N*-tosylaziridinofullerene with thioureas or guanidines is developed.
2. The reaction exhibits excellent chemoselectivity for the unsymmetrical thioureas.
3. An unusual reaction of cyclic guanidine fused C_{60} with CS_2 is observed.