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REACTION OF [60]FULLERENE WITH EPOXIDES UNDER PHOTO-IRRADIATION: SYNTHESIS OF C₆₀-FUSED TETRAHYDROFURAN DERIVATIVES

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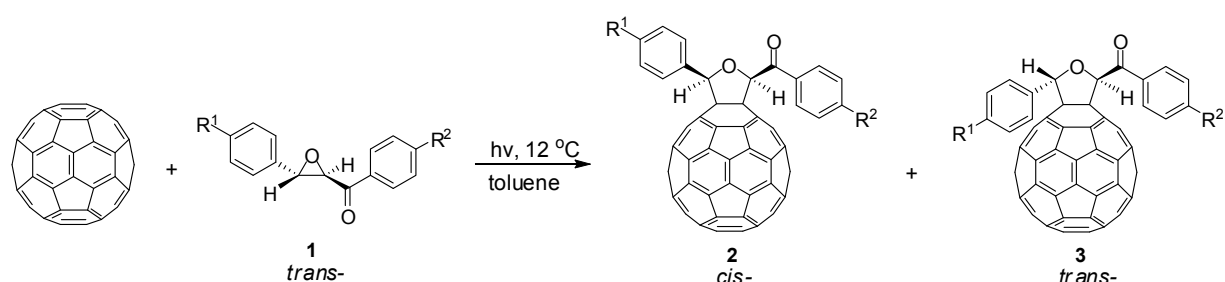
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Abstract – The photoreactions of [60]fullerene (C₆₀) with various epoxides have been investigated. *Trans* 2-aryloxy-3-aryloxiranes reacted with [60]fullerene giving both the major *cis* products and the minor *trans* adducts. The influence of substituent group on aryl ring on the photoreaction is entirely different from that of preliminary reported thermal reaction. In addition, the photo condition could avoid the decomposition of some original epoxides compared to the thermal condition at high temperature. It provides a simple and efficient route to synthesize C₆₀-fused tetrahydrofuran derivatives.

Fullerene derivatives possess potential applications in material science and medicinal chemistry.¹ The 1,3-dipolar cycloaddition reaction is one of the most useful methodologies for the functionalization of fullerenes. Various 1,3-dipoles including azomethine ylides, diazo compounds, azides, nitrile oxides, nitrile ylides, nitrile imine, pyrazolinium ylides have been reported to react with fullerenes.² Epoxides undergoing thermal or photochemical 1,3-dipolar cycloaddition *via* carbonyl ylides with alkenes,³ alkynes,⁴ benzylidene anilines,⁵ thioketones,⁶ phosphalkynes⁷ have been well explored. However, carbonyl ylides as 1, 3-dipoles applied to the functionalization of C₆₀ are seldom investigated. Jagerovic first reported the TCNE oxide serving as a carbonyl ylide to react with C₆₀.⁸ Nair and coworkers have shown that cyclic carbonyl ylides generated *in situ* from diazo ketones in the presence of Rh₂(OAc)₄ undergo facile dipolar cycloaddition with C₆₀ affording novel organofullerenes.⁹ In a preliminary report two of us have investigated the reaction of [60]fullerene (C₆₀) with the carbonyl ylides generated *in situ*

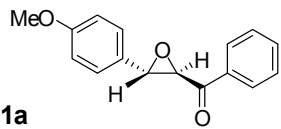
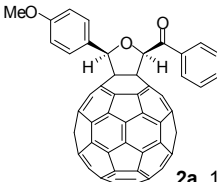
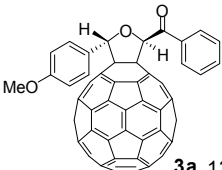
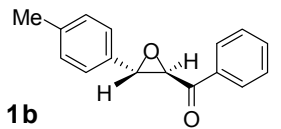
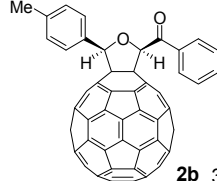
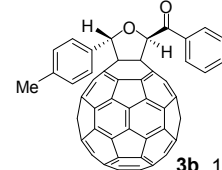
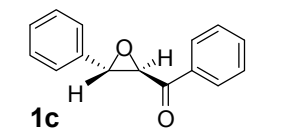
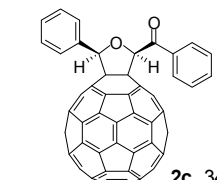
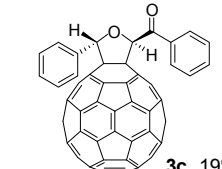
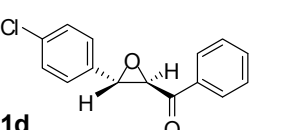
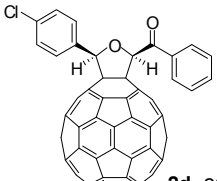
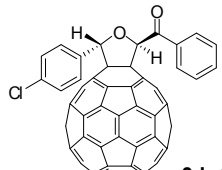
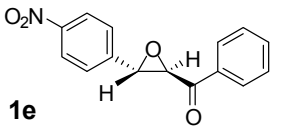
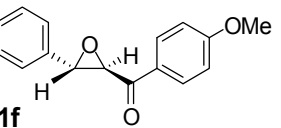
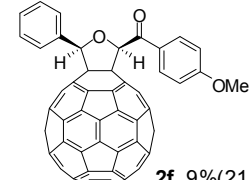
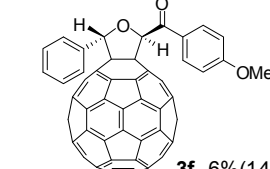
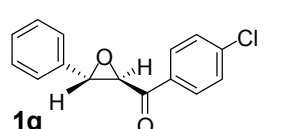
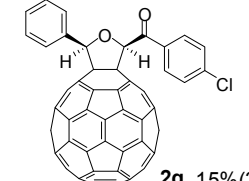
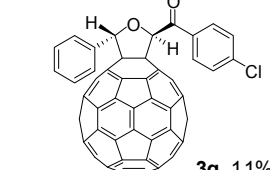
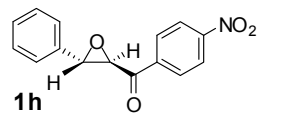
from *trans* epoxides under thermal condition.¹⁰ The thermal reaction of C₆₀ with *trans* epoxides afforded exclusively or predominantly the *cis* isomers of C₆₀-fused tetrahydrofuran derivatives containing functional groups such as ketone, ester and cyano groups. According to Woodward-Hoffmann rules for electrocyclic ring opening in four-electron systems, C-C bond cleavage of the *trans* oxiranes under thermal or photo condition will give different 1,3-dipoles which may result in the difference in the isomeric distribution of addition product.^{11,12} We here present the reaction of [60]fullerene with *trans* epoxides under photo-irradiation.



Scheme 1. Photoreaction of C₆₀ with *trans*-2-aryl-3-aryl oxiranes

We firstly investigated the photoreaction of C₆₀ with typical *trans* oxiranes **1a-h**, which were prepared according to the reported procedure¹¹ (Scheme 1). The mixture of C₆₀ with *trans* oxiranes **1a-h** in toluene were photoirradiated with 250 W high-voltage mercury lamp at 12 °C, respectively. The reaction time and yields were outlined in Table 1. Theoretically, *trans* product **3** would be the only product because photochemical disrotatory opening of the *trans* epoxides leads to a *trans* carbonyl ylide whose geometry would be preserved after cycloaddition with C₆₀. Surprisingly, for substrates **1a-d** and **1f-g**, not only *trans* products **3a-d** and **3f-g** but also unexpected *cis* products **2a-d** and **2f-g** were afforded while in the thermal reaction only the *cis* products could be obtained. Moreover, the *cis* isomers were the major products. It could be explained by that the C-O bond rotation of *trans* carbonyl ylide would lead to *cis* carbonyl ylide, which reacted with C₆₀ to give more stable *cis* product because the aryl and benzoyl groups are both in the equatorial position. The results were entirely different from our forecast. The isomeric distribution of **2a-d**, **2f-g** and **3a-d**, **3f-g** was seldom affected by the electronic property of the substituent on the phenyl ring. However, the reaction rate was dramatically affected by the substituents R¹ and R² on the phenyl ring. R¹ had great influence on the reaction rate whereas R² had significant influence on the yield. When R² was H, whether R¹ was weak electron-withdrawing or electron-donating group the reaction gave satisfactory yields. Electron-donating group R¹ on the aryl ring such as OMe accelerated the reaction greatly (Table 1, entry 1). On the contrary, no product was observed under thermal reaction when R¹ was OMe due to the decomposition of corresponding epoxide. It should be noted that no reaction occurred when R¹ or R² was strong withdrawing group NO₂ even after prolonging the reaction time to 48 h (Table

Table 1. Yields and reaction time for the reaction of C₆₀ with **1a-h** under photoirradiation at 12 °C

Entry	Substrate	Time	Products and Yields ^a	
1		8 h	 2a , 18%(29%)	+  3a , 13%(20%)
2		20 h	 2b , 31%(42%)	+  3b , 19%(25%)
3		40 h	 2c , 34%(63%)	+  3c , 19%(35%)
4		40 h	 2d , 20%(43%)	+  3d , 13%(27%)
5		48 h	N. R.	
6		20 h	 2f , 9%(21%)	+  3f , 6%(14%)
7		20 h	 2g , 15%(32%)	+  3g , 11%(24%)
8		48 h	N. R.	

^a Isolated yield, that in the parenthesis refers to the yield based on consumed C₆₀.

1, entry 5, 8) whereas the same reaction proceeded well when R¹ was NO₂ under thermal condition. When R² on the aryl ring changed from H to OMe or Cl the yields decreased notably (Table 1, entry 6, 7).

The structures of **2a**, **2d**, **2f**, **2g**, **3a-d**, **3f** and **3g** were fully identified by their MS, ¹H NMR, ¹³C NMR, FT-IR and UV-vis spectra. The *cis* stereochemistry of **2** was substantiated by the NOESY spectrum.¹⁰ The ¹H NMR spectral patterns of isomeric **3** and **2** were very similar, the only noticeable difference was a downfield shift of 0.68-0.88 ppm for the two methine hydrogen of **3** (**3a**, **3d**, **3f**, **3g** vs. **2a**, **2d**, **2f**, **2g**) in the ¹H NMR spectrum. For example, **2a** and **3a** allowed the assignment of all chemical shifts in their ¹H NMR and ¹³C NMR spectra in CS₂-CDCl₃, as shown in Figure 1. Hydrogen bond must be existed between the H_a and carbonyl oxygen, which caused the downfield shifts¹³ of 0.87 ppm for H_a and 3.19 ppm for the carbonyl group in the ¹H NMR spectrum and ¹³C NMR spectrum of *trans* isomers relative to the *cis* isomers, respectively. The observed red shift of 6 cm⁻¹ for the absorption of the carbonyl group in compounds **3a** relative to **2a** (1684 cm⁻¹ for **3a** vs 1690 cm⁻¹ for **2a**) also proved the existence of hydrogen bond. The downfield shifts of 0.68 ppm for H_b in the ¹H NMR spectrum may be induced by the change of H_b from axial position to equatorial position. Thus, adducts **2a-d** are *cis* isomers, and compounds **3a-d** have *trans* structures. Similar phenomena for the ¹H and ¹³C NMR downfield shifts was also observed in previous report.^{10,14}

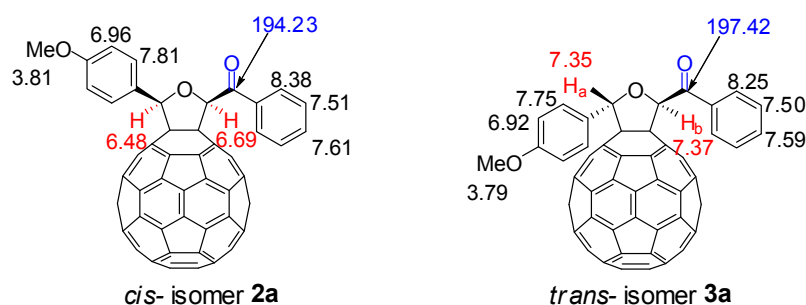


Figure 1. The obvious difference of NMR spectra data between *cis*-isomer and *trans*-isomer

In order to study the application universality of the photoreaction we next examined many other substrates **4-9** (Figure 2). We firstly took the *trans*-2-cyano-2-ethoxycarbonyl-3-phenyl oxirane **4** as a try. Although oxirane **4** reacted well with C₆₀ under thermal condition, no reaction was observed under photo-irradiation. It was conjectured that the strong electron-withdrawing group (CN) may be an unfavourable factor. Therefore, **5** was chosen to react with C₆₀ under photo condition. To our disappointment, **5** also did not react with C₆₀. Furthermore, we investigated the photoreaction of oxiranes **6-9** with C₆₀. No any desired cycloaddition reactions occurred yet. From these results, it was concluded that the two aryl rings and carbonyl group in the structure of **1** are essential to the photoreaction.

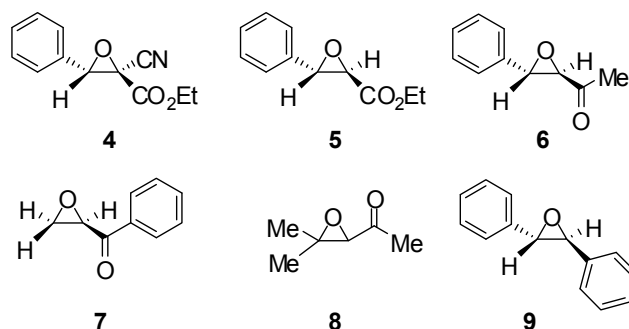


Figure 2. Different kinds of epoxides

In summary, the photoreaction of C_{60} with *trans* epoxides to give C_{60} -fused tetrahydrofuran derivatives has been investigated. Not only the major *cis* products but also the minor *trans* products could be obtained from the photoreaction while only *cis* product could be obtained in the preliminary reported thermal reaction. The isomer distribution was seldom affected by the substituent on the phenyl ring. The influence of substituent on phenyl ring on the photoreaction was entirely different from the thermal reaction. In addition, the photo condition could avoid the decomposition of some original epoxides compared to the thermal condition at high temperature. It provided a simple and efficient methodology to synthesize C_{60} -fused tetrahydrofuran derivatives.

EXPERIMENTAL

General procedure for the reaction of C_{60} with *trans* 2-benzoyl-3-aryl oxiranes 1a-d. A mixture of C_{60} (54.0 mg, 0.075 mmol) and **1a-1d**, (0.3 mmol) was dissolved in toluene (60 mL) in a big glass tube (25×250 mm), then the tube was immersed in flowing water and photo-irradiated with 250 W high-voltage mercury lamp at 12 °C for the designated time. The solvent was then evaporated *in vacuo*, and the residue was separated on a silica gel column eluted with CS_2 or CS_2 -toluene mixture to afford unreacted C_{60} , **2a-d** and **3a-d**. The spectra data and spectra could be seen in supporting information.

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