HETEROCYCLES, Vol. 83, No. 7, 2011, pp. 1615 - 1620. © The Japan Institute of Heterocyclic Chemistry
Received, 10th February, 2011, Accepted, 11th April, 2011, Published online, 19th April, 2011
DOI: 10.3987/COM-11-12170

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

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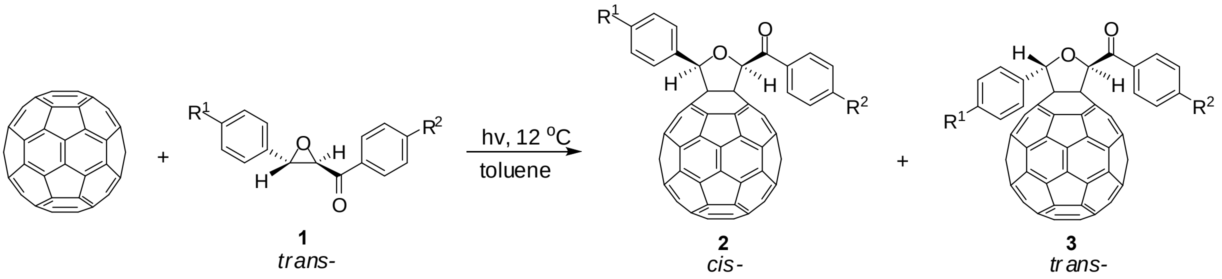
Abstract – The photoreactions of [60]fullerene (C_{60}) with various epoxides have been investigated. *Trans* 2-aroyl-3-aryloxiranes reacted with [60]fullerene giving both the major *cis* products and the minor *trans* adducts. The influence of substituent group on aryl ring on the photoreaction is entirely 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 C_{60}-fused tetrahydrofuran derivatives.

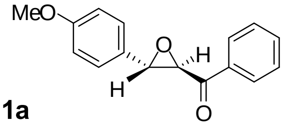
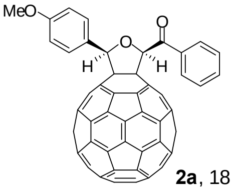
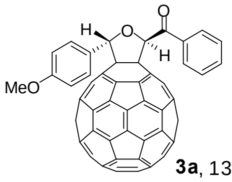
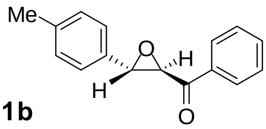
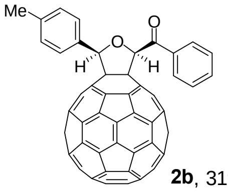
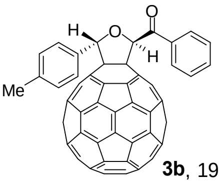
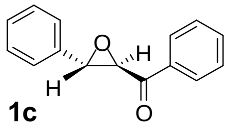
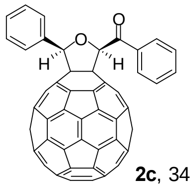
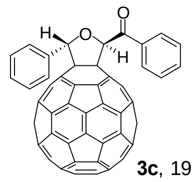
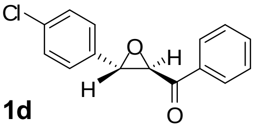
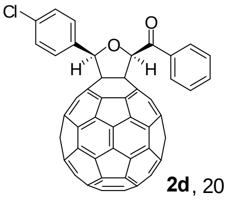
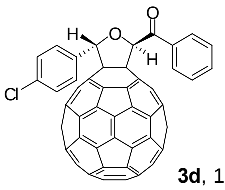
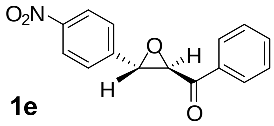
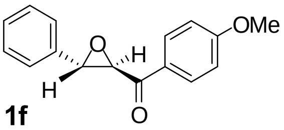
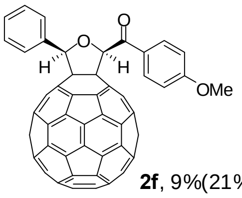
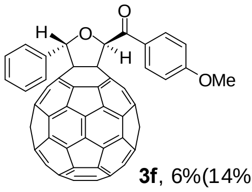
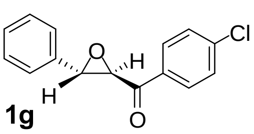
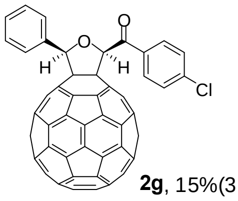
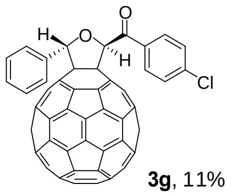
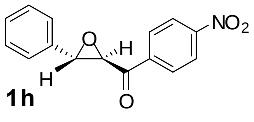
Fullerene derivatives possess potential applications in material science and medicinal chemistry.[1] The 1,3-dipolar cycloaddition reaction is one of the most useful methodologies for the functionalization of fullerenes. Various 1,3-dipoles including azomethine ylides, diazo compounds, azides, nitrile 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] phosphaalkynes[7] have been well explored. However, carbonyl ylides as 1, 3-dipoles applied to the functionalization of C_{60} are seldom investigated. Jagerovic first reported the TCNE oxide serving as a carbonyl ylide to react with C_{60}.[8] Nair and coworkers have shown that cyclic carbonyl ylides generated *in situ* from diazo ketones in the presence of $Rh_2(OAc)_4$ undergo facile dipolar cycloaddition with C_{60} affording novel organofullerenes.[9] In a preliminary report two of us have investigated the reaction of [60]fullerene (C_{60}) with the carbonyl ylides generated *in situ* from *trans* epoxides under thermal condition.[10] The thermal reaction of C_{60} with *trans* epoxides afforded exclusively or predominantly the *cis* isomers of C_{60}-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 C_{60} with *trans*-2-aroyl-3-aryl oxiranes

We firstly investigated the photoreaction of C_{60} with typical *trans* oxiranes **1a-h**, which were prepared according to the reported procedure[11] (Scheme 1). The mixture of C_{60} 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 C_{60}. 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 C_{60} 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 R^1 and R^2 on the phenyl ring. R^1 had great influence on the reaction rate whereas R^2 had significant influence on the yield. When R^2 was H, whether R^1 was weak electron-withdrawing or electron-donating group the reaction gave satisfactory yields. Electron-donating group R^1 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 R^1 was OMe due to the decomposition of corresponding epoxide. It should be noted that no reaction occurred when R^1 or R^2 was strong withdrawing group NO_2 even after prolonging the reaction time to 48 h (Table

Table 1. Yields and reaction time for the reaction of C_{60} with **1a-h** under photoirradiation at 12 °C

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

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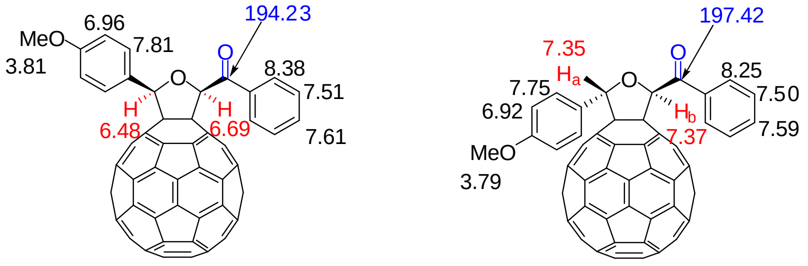
[a] Isolated yield, that in the parenthesis refers to the yield based on consumed C_{60}.

1, entry 5, 8) whereas the same reaction proceeded well when R^1 was NO_2 under thermal condition. When R^2 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, ^{13}C 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, 3f** 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 ^{13}C NMR spectra in CS_2-$CDCl_3$, as shown in Figure 1. Hydrogen bond must be existed between the H_a and carbonyl oxygen, which caused the downfield shifts[13] of 0.87 ppm for H_a and 3.19 ppm for the carbonyl group in the ^1H NMR spectrum and ^{13}C 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 ^{13}C NMR downfield shifts was also observed in previous report.[10,14]



cis- isomer **2a**   *trans*- isomer **3a**

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 C_{60} 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 C_{60} under photo condition. To our disappointment, **5** also did not react with C_{60}. Furthermore, we investigated the photoreaction of oxiranes **6-9** with C_{60}. 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.

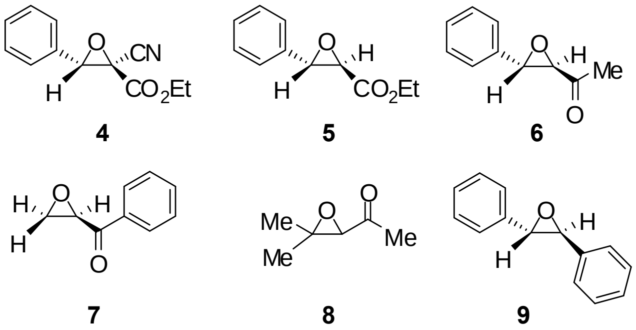


Figure 2. Different kinds of epoxides

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 ^{o}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.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China (Nos. 20902039 and 20872051) and Natural Science Foundation of Jiangsu Province (BK2009543).

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