Tetrahedron 70 (2014) 5828–5833

Contents lists available at ScienceDirect

Tetrahedron

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

# Facile and efficient synthesis of fluorinated fullerene-fused 1,3-dioxolanes: reaction of $C_{60}$ with fluorinated aromatic aldehyde mediated by lithium perchlorate

Hao-Nan Cheng [a], Yuan-Hai Zou [a], Jian-Min Zhang [a,b,*], Shan-Shan He [a], Su-Bo Shen [a], Hong-Mei Deng [c]

[a] Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, PR China
[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China
[c] Center of Analysis and Test, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

*Article history:*
Received 8 April 2014
Received in revised form 2 June 2014
Accepted 10 June 2014
Available online 16 June 2014

*Keywords:*
Fullerene
Lithium perchlorate
Ionic reaction
Fluorine
Cyclic voltammetry

ABSTRACT

A series of fluorinated fullerene-fused 1,3-dioxolanes have been facilely and efficiently synthesized in the presence of easily available $LiClO_4 \cdot 3H_2O$. The influences of the number of fluoro-substituents and their positions linked to the phenyl ring on the isolated yield of fullerene-fused 1,3-dioxolanes have been studied in detail. Based on reaction facts, a possible reaction mechanism for the formation of fluorinated fullerene-fused 1,3-dioxolanes has been proposed. Furthermore, detailed ultraviolet absorption spectra, fluorescence emission spectra, and cyclic voltammogram further explain the optical properties and electronic transmission capabilities of the products.



## 1. Introduction

Since the discovery by Kratschmer et al. of a method to prepare macroscopic quantities of $C_{60}$ in 1990s,[1] the functionalization of $C_{60}$ has become one of the hottest areas in current research. Heterocyclic derivatives of fullerene $C_{60}$ have aroused great interest due to their structural and functional diversities. The well-known Prato reaction has been widely used to functionalize fullerene $C_{60}$ via 1,3-dipolar cycloaddition. $C_{60}$-fused lactones prepared by manganese(III) acetate mediated cycloaddition have been reported by Wang et al. in 2006, and a novel reductive ring opening process was disclosed.[1] The carbonyl ylides generated in situ from *trans*-epoxides were also used to prepare $C_{60}$-fused tetrahydrofuran derivatives by the same research group. The introduction of fluorine atoms or fluorine-containing groups into the substrate would have profound effect on reactivity and therefore reaction conditions and mechanisms. Although fluoro or trifluoromethyl derivatives of $C_{60}$ have been investigated for many years,[2,3] there seems to be limited reports on this system. Recently, vast efforts have been devoted to exploring and improving the protocols for the preparation of fluorinated $C_{60}$ derivatives in our group. Two interesting types of heterocycle-containing $C_{60}$ derivatives, fullerene-fused fluorine-containing lactones and pentafluorinated phenyl-monohydro[60] fullerenes have been obtained.[4]

Lewis acid catalyst has been widely used in organic transformations.[5] A straightforward preparation of $C_{60}$-fused 1,3-dioxolane derivatives promoted by $Fe(ClO_4)_3 \cdot 6H_2O$ has been successfully applied by Wang et al.,[6] and $LiClO_4 \cdot 3H_2O$ assisted 1,3-dipolar cycloaddition of azomethine ylides to $C_{60}$ was reported by Ioutsi et al.[7] In terms of activity-per-gram, fluorinated compounds are frequently more effective and are required in smaller quantities than non-fluorinated compounds. So far, for the introduction of fluorine atom into fullerene derivatives, it is not very clear how the fluorine atom influencing on the reaction protocols, i.e., the reaction temperature,[4] the yield, or the quantities of reactants. Moreover, while there are reports of fluorinated fullerene-fused 1,3-dioxolanes as heterocyclic fluorine-containing fullerene derivatives, the number of these compounds is limited in the reports, thus further studies are required.[8] All of the above considerations inspired us to study the suitable conditions for the preparation of $C_{60}$-fused 1,3-dioxolane derivatives with $C_{60}$ and aldehydes in the presence of $LiClO_4 \cdot 3H_2O$.

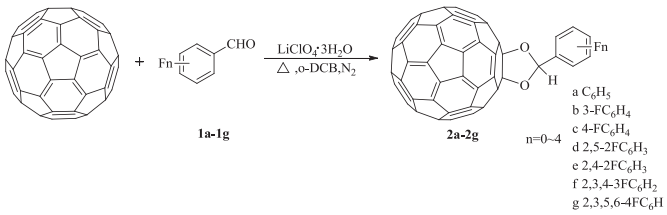
* Corresponding author. Tel./fax: +86 21 66133801; e-mail addresses: jmzhang@shu.edu.cn (J.-M. Zhang), bobobao1989@shu.edu.cn (S.-B. Shen).

http://dx.doi.org/10.1016/j.tet.2014.06.038
0040-4020/

## 2. Results and discussion

Herein, the reaction of $C_{60}$ with various kinds of fluorinated aldehydes could be promoted by $LiClO_4 \cdot 3H_2O$ to yield fluorinated fullerene-fused 1,3-dioxolanes. Furthermore, a possible reaction mechanism has been proposed according to the experimental results.

The synthetic route is depicted in Scheme 1, 2,4-difluorobenzaldehyde(**1e**) was chosen to illustrate the optimization of the reaction conditions, and the results were summarized in Table 1. Optimizations were conducted by varying the catalyst, molar ratio, and the reaction temperature. Only trace of product was detected when $FeCl_3$ or $HClO_4$ was used as the catalyst. Surprisingly, the reaction promoted by $LiClO_4 \cdot 3H_2O$ was carried out smoothly. For comparison, compound **1e** was also treated with $C_{60}$ in the presence of $Fe(ClO_4)_3 \cdot 6H_2O$, and the reaction was performed under the conditions reported by Wang et al.[6] With a slightly higher temperature, a yield of 36% was achieved, and this is relatively lower than that of the reaction promoted by $LiClO_4 \cdot 3H_2O$ (Table 1, entries 3 and 12). Then, we rechecked the reaction under herewith optimized conditions by using $Fe(ClO_4)_3 \cdot 6H_2O$ instead of $LiClO_4 \cdot 3H_2O$, and the trace of a product was detected in prolonged reaction time. The reaction of fluorinated benzaldehyde with $C_{60}$ was found to occur at a higher temperature (130 °C) than that of benzaldehyde, which occurs at 80 °C.[6] Furthermore, the reaction temperatures above or below 130 °C would lead to decreasing of the product yield (Table 1, entries 9 and 10). The best molar ratio of $C_{60}$/$LiClO_4 \cdot 3H_2O$/**1e** was 1:11:12, below this the product yield can be improved (from 24% to 51%) by increasing the amount of $LiClO_4 \cdot 3H_2O$ and **1e**, however, when the ratio of $LiClO_4 \cdot 3H_2O$ was increased to 12 and the ratio of **1e** to 13 the yields decreased (Table 1, entries 4 and 6). Due to the high reaction temperature in our system, we selected *o*-dichlorobenzene as the solvent, instead of toluene, which has been widely used in the reactions involving the modification of $C_{60}$.




**Scheme 1.** Synthesis of fluorinated fullerene-fused 1,3-dioxolanes **2**.

**Table 1**
Optimization of reaction conditions for the reaction of $C_{60}$ with 2,4-difluorobenzaldehyde **1e**

| Entry | Catalyst | Molar ratio[a] | Time (h) | *T* (°C) | Yield of **2e**[b] |
|---|---|---|---|---|---|
| 1 | $LiClO_4 \cdot 3H_2O$ | 1:10:5 | 2.5 | 130 | 31(38) |
| 2 | $LiClO_4 \cdot 3H_2O$ | 1:10:12 | 2.5 | 130 | 32(40) |
| 3 | $LiClO_4 \cdot 3H_2O$ | 1:11:12 | 2.5 | 130 | 51(71) |
| 4 | $LiClO_4 \cdot 3H_2O$ | 1:12:12 | 2.5 | 130 | 48(68) |
| 5 | $LiClO_4 \cdot 3H_2O$ | 1:11:11 | 2.5 | 130 | 39(65) |
| 6 | $LiClO_4 \cdot 3H_2O$ | 1:11:13 | 2.5 | 130 | 29(37) |
| 7 | $LiClO_4 \cdot 3H_2O$ | 1:11:12 | 2 | 130 | 40(61) |
| 8 | $LiClO_4 \cdot 3H_2O$ | 1:11:12 | 3 | 130 | 48(59) |
| 9 | $LiClO_4 \cdot 3H_2O$ | 1:11:12 | 2.5 | 120 | 29(48) |
| 10 | $LiClO_4 \cdot 3H_2O$ | 1:11:12 | 2.5 | 140 | 41(61) |
| 11 | $Fe(ClO_4)_3 \cdot 6H_2O$ | 1:11:12 | 2.5 | 130 | Trace |
| 12 | $Fe(ClO_4)_3 \cdot 6H_2O$ | 1:2:5 | 1.5 | 100 | 36(50) |
| 13 | $HClO_4$ | 1:11:12 | 2.5 | 130 | Trace |
| 14 | $FeCl_3$ | 1:11:12 | 2.5 | 130 | Trace |

[a] Molar ratio of $C_{60}$/catalyst/**1e**.
[b] The number in parentheses is the isolated yield based on consumed $C_{60}$.

In the following investigations, we carried out parallel reactions catalyzed by $Fe(ClO_4)_3 \cdot 6H_2O$ and $LiClO_4 \cdot 3H_2O$ under their own optimized reaction conditions, respectively. In view of the reaction temperature and the yield of these two systems (Table 2), it is clear that our system catalyzed by $LiClO_4 \cdot 3H_2O$ could be more attractive considering the relatively higher yields.

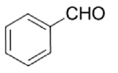
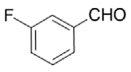
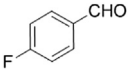
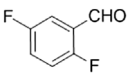
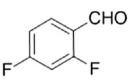
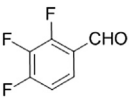
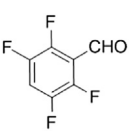
**Table 2**
Comparisons of the reaction catalyzed by $Fe(ClO_4)_3 \cdot 6H_2O$ and $LiClO_4 \cdot 3H_2O$

| Entry[a] | Aldehyde **1** | $Fe(ClO_4)_3 \cdot 6H_2O$ | | $LiClO_4 \cdot 3H_2O$ | |
|---|---|---|---|---|---|
| | | *T* (°C) | Yield[b] | *T* (°C) | Yield[b] |
| 1 | **1a** | 80 | 34(85) | 110 | 51(73) |
| 2 | **1b** | 100 | 27(62) | 130 | 40(60) |
| 3 | **1c** | 100 | 25(37) | 130 | 42(79) |
| 4 | **1d** | 100 | 24(42) | 130 | 48(76) |
| 5 | **1e** | 100 | 36(50) | 130 | 51(71) |

[a] Molar ratio of $C_{60}$/$LiCO_4 \cdot 3H_2O$/**1**=1:11:12; molar ratio of $C_{60}$/$Fe(ClO_4)_3 \cdot 6H_2O$/**1**=1:2:5.
[b] The number in parentheses is the isolated yield based on consumed $C_{60}$. The yield of product **1a** was cited from the related literature.[6]

Various kinds of fluoro-substituted aromatic aldehydes were selected as substrates as shown in Table 3. The feasibility of this kind of reaction may refer to the successful preparation of fluorine-containing fullerene-fused 1,3-dioxolanes. For all fluoro-substituted aromatic aldehydes, the yields were moderate, ranging from 28% to 51%. A relatively high yield was achieved when 2,4-difluorobenzadehyde or 2,5-difluorobenzadehyde was used as the substrate, while the relatively low one has been observed for the multi-fluoro-substituted substrate. The isolated yields were largely affected by the number of fluoro-substituents and their positions on phenyl ring as well. We could obtain over 40% yield based on

**Table 3**
The reaction conditions and yields for the reactions of $C_{60}$ with fluorinated aldehydes

| Entry[a] | Aldehyde **1** | Structure | Time (h) | *T* (°C) | Yield[b] |
|---|---|---|---|---|---|
| 1 | **1a** |  | 2.5 | 110 | 51(73) |
| 2 | **1b** |  | 2.5 | 130 | 40(60) |
| 3 | **1c** |  | 2.5 | 130 | 42(79) |
| 4 | **1d** |  | 2.5 | 130 | 48(76) |
| 5 | **1e** |  | 2.5 | 130 | 51(71) |
| 6 | **1f** |  | 2.5 | 130 | 28(42) |
| 7 | **1g** |  | 2.5 | 140 | 30(41) |

[a] Molar ratio of $C_{60}$/$LiCO_4 \cdot 3H_2O$/**1**=1:11:12.
[b] The number in parentheses is the isolated yield based on consumed $C_{60}$.