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Synthesis of Fullerene-Fused Dioxanes/Dioxepanes: Ferric Perchlorate-Mediated One-Step Reaction of [60]Fullerene with Diols

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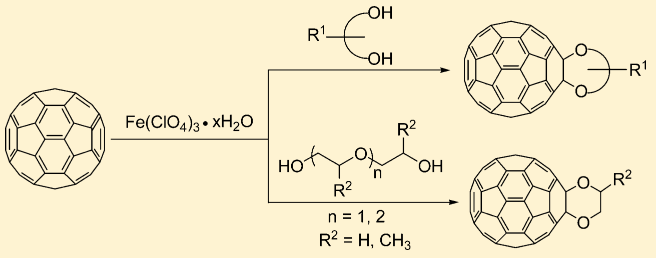
Supporting Information

ABSTRACT: The facile one-step reaction of [60]fullerene with various diols in the presence of ferric perchlorate afforded a series of rare fullerene-fused dioxanes/dioxepanes. Nevertheless, the reaction of [60]fullerene with diethylene glycol, triethylene glycol, and tripropylene glycol promoted by ferric perchlorate unexpectedly generated fullerene-fused dioxanes instead of the anticipated fullerene-fused crown ethers. A plausible reaction mechanism is proposed to explain the formation of fullerene-fused dioxane/dioxepane products.



INTRODUCTION

Many chemical reactions have been discovered over the past two decades, and a large number of fullerene derivatives with many structural diversities have been prepared.[1] Cycloadditions are the most studied fullerene reactions,[1a,b] and many functional groups can be covalently linked to fullerenes by means of cycloadditions with suitable addends. For example, cycloadditions of [60]fullerene (C_{60}) with aldehydes/ketones promoted by metal salts could afford a series of fullerene-fused 1,3-dioxolanes.[2] In comparison with the extensively reported fullerene-fused 1,3-dioxolanes, fullerene-fused dioxane/dioxepane derivatives have been relatively rare. Until now, only three examples of fullerene-fused dioxanes/dioxepanes have been reported via a two-step reaction starting from C_{60}, that is, transetherification of fullerenyl boronic esters with diols in the presence of *p*-toluenesulfonic acid.[3] This methodology for the preparation of fullerene-fused dioxanes/dioxepanes is indirect and requires a large excess of diols (50 equiv). Therefore, there is still a demand to develop a new protocol to obtain fullerene-fused dioxane/dioxepane derivatives directly from C_{60} in a straightforward and efficient way with a broad substrate scope.

Recently, transition-metal-salt-mediated radical reactions of fullerenes have attracted tremendous attention.[4] Diverse types of transition metal salts such as those of Mn,[5] Fe,[2a,3,6,7] W,[8] Cu,[9] Pb,[10] Co,[11] and Ag[12] have been utilized as the promoters to functionalize fullerenes. Compared with the traditional peroxide- or light-initiated processes, the radical reactions of fullerenes promoted by transition metal salts could proceed well under mild conditions and tend to give a monoaddition product that is relatively easy to isolate and purify, through which numerous novel monoaddition fullerene derivatives have been prepared. For instance, the $Fe(ClO_4)_3$-mediated radical reactions of C_{60} with nitriles,[6a] aldehydes/ketones,[2a] malonate esters,[6b] arylboronic acids,[3] acid chlorides,[6c] β-keto esters,[6d] and isocyanates/isothiocyanates[6e] afforded a large variety of novel fullerene derivatives, including oxazolines, 1,3-dioxolanes, disubstituted C_{60}-fused lactones, boronic esters, 1,2-fullerenols, hemiketals, and oxazolidinofullerenes/thiazolidinofullerenes. In continuation of our interest in fullerene chemistry, herein we describe a one-step reaction of C_{60} with diols promoted by cheap and easily available $Fe(ClO_4)_3$ to afford a variety of interesting fullerene-fused dioxanes/dioxepanes.

RESULTS AND DISCUSSION

Ethylene glycol (**1a**) was first chosen to react with C_{60} in the presence of $Fe(ClO_4)_3$. At the onset, the mixture of C_{60} (0.05 mmol), $Fe(ClO_4)_3$ (0.10 mmol), and ethylene glycol (0.25 mmol) was dissolved in a single solvent, that is, *o*-dichlorobenzene (ODCB, 6 mL), and the resulting solution was heated with vigorous stirring in an oil bath preset at 100 °C under nitrogen atmosphere for 24 h. We found that a significant amount of byproducts with polarity similar to that of C_{60} was always concurrently formed, although the desired fullerene-fused dioxane **2a** was obtained in 17% isolated yield (entry 1, Table 1). To improve the yield and selectivity of this reaction, various reaction conditions have been examined. To our delight, the reaction was found to successfully avoid the formation of the above byproducts and to give fullerene-fused dioxane **2a** in 21% yield when the mixture of C_{60}, $Fe(ClO_4)_3$, and ethylene glycol was dissolved in a mixed solvent, such as ODCB (6 mL) and acetonitrile (CH_3CN, 2 mL) (entry 2, Table 1). Increasing or decreasing the reaction temperature did not improve the yield of product **2a** (entries 3 and 4, Table 1). The variation of the amount of $Fe(ClO_4)_3$ (from 1 to 3 equiv) and ethylene glycol (from 2 to 8 equiv) had also no benefit to

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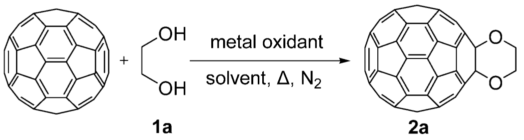
Table 1. Optimization of Reaction Conditions for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Ethylene Glycol 1a[a]



entry	metal oxidant	molar ratio[b]	solvent	temp (°C)	time (h)	yield (%) of 2a[c]
1	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	ODCB	100	24	17 (30)
2	$\mathbf{Fe(ClO_4)_3{\cdot}xH_2O}$	**1:2:5**	**ODCB/CH_3CN**	**100**	**24**	**21 (88)**
3	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	ODCB/CH_3CN	120	24	18 (67)
4	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	ODCB/CH_3CN	80	24	15 (94)
5	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:5	ODCB/CH_3CN	100	24	14 (88)
6	$Fe(ClO_4)_3{\cdot}xH_2O$	1:3:5	ODCB/CH_3CN	100	24	19 (63)
7	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:2	ODCB/CH_3CN	100	19	15 (54)
8	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:8	ODCB/CH_3CN	100	24	20 (83)
9[d]	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	ODCB/CH_3CN	100	24	18 (64)
10	$FeCl_3{\cdot}6H_2O$	1:2:5	ODCB/CH_3CN	100	24	10 (91)
11	$FeCl_3$	1:2:5	ODCB/CH_3CN	100	24	10 (91)
12	$CuCl_2{\cdot}2H_2O$	1:2:5	ODCB/CH_3CN	100	24	10 (91)
13	$CuCl_2$	1:2:5	ODCB/CH_3CN	100	24	9 (90)
14	$Mg(ClO_4)_2$	1:2:5	ODCB/CH_3CN	100	24	0
15	$Mn(OAC)_3{\cdot}H_2O$	1:2:5	ODCB/CH_3CN	100	24	0
16	$Cu(OAC)_3{\cdot}H_2O$	1:2:5	ODCB/CH_3CN	100	24	0
17	$Pb(OAC)_4$	1:2:5	ODCB/CH_3CN	100	24	0
18	$(NH_4)_2Ce(NO_3)_6$	1:2:5	ODCB/CH_3CN	100	5	0
19	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	ODCB/DMSO	100	24	0
20	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	ODCB/DMF	100	24	0

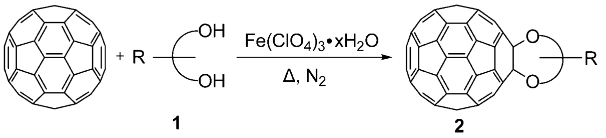
[a] All reactions were performed under nitrogen conditions unless otherwise indicated. [b] Molar ratio refers to $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/$**1a**. [c] Isolated yield; those in parentheses were based on consumed C_{60}. [d] To prepare **2a** on a larger scale, 216 mg of C_{60} was used.

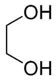
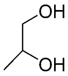
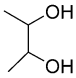
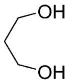
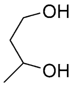
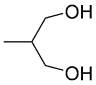
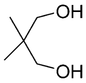
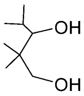
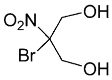
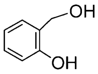
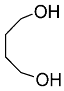
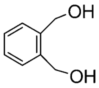
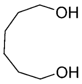
the isolated yield of product **2a** (entries 5−8, Table 1). Therefore, the reagent molar ratio of 1:2:5 ($C_{60}/Fe(ClO_4)_3/$**1a**), the reaction temperature of 100 °C, and the reaction solvent of ODCB/CH_3CN were chosen as the optimized reaction conditions. To ensure the yields listed in Table 1 are accurate, the reaction of C_{60}, $Fe(ClO_4)_3$, and ethylene glycol was further conducted on a larger scale. For example, 216 mg of C_{60} was employed to react with ethylene glycol and $Fe(ClO_4)_3$ under the optimized conditions and was found to afford 18% yield of **2a** (entry 9, Table 1), which is slightly lower than that from 36 mg of C_{60} (entry 9 vs entry 2, Table 1). It should be noted that other metal oxidants such as $FeCl_3{\cdot}6H_2O$, $FeCl_3$, $CuCl_2{\cdot}2H_2O$, $CuCl_2$, $Mg(ClO_4)_2$, $Cu(OAc)_2{\cdot}H_2O$, $Mn(OAc)_3{\cdot}2H_2O$, $Pb(OAc)_4$, and $(NH_4)_2Ce(NO_3)_6$ were also examined under the optimized conditions (entries 10−18, Table 1). Unfortunately, these metal oxidants instead of $Fe(ClO_4)_3$ only led to the formation of about 10% or no yield of product **2a**, and thus $Fe(ClO_4)_3$ has been proven to be the best oxidant. In addition, other polar solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) in place of CH_3CN were also investigated (entries 19 and 20, Table 1). To our disappointment, no obvious reaction was observed under the standard reaction conditions.

With the optimized conditions in hand, this reaction could be extended to other diols such as 1,2-propanediol (**1b**), 2,3-butanediol (**1c**), 1,3-propanediol (**1d**), 1,3-butanediol (**1e**), 2-methyl-1,3-propanediol (**1f**), 2,2-dimethyl-1,3-propanediol (**1g**), 2,2,4-trimethyl-1,3-pentanediol (**1h**), and 2-bromo-2-nitro-1,3-propanediol (**1i**) and were found to generate the desired fullerene-fused dioxanes/dioxepanes **2b**−**i**, respectively. Additionally, 2-hydroxybenzenemethanol (**1j**), 1,4-butanediol (**1k**), 1,2-benzenedimethanol (**1l**), and 1,6-hexanediol (**1m**) were also investigated. The reaction conditions and yields for the $Fe(ClO_4)_3$-mediated reactions to C_{60} and diols **1a**−**m** are summarized in Table 2.

As can be seen from Table 2, all of the examined diols **1a**−**i** could be successfully employed to prepare fullerene-fused dioxanes/dioxepanes **2a**−**i** in 20−34% isolated yields (70−97% based on consumed C_{60}), comparable to the previously reported data for most monoadducts. For the synthesis of fullerene-fused dioxanes **2b** and **2c**, increasing the amount of diols **1b** and **1c** from 5 to 10 equiv could provide an acceptable product yield in 22% and 25%, respectively. For the preparation of fullerene-fused dioxepane **2i**, higher product yield (34%) together with shorter reaction time (7 h) was observed, probably due to the higher reactivity of 2-bromo-2-nitro-1,3-propanediol (**1i**) bearing the strong electron-withdrawing NO_2 and Br groups. It is noteworthy that functional groups such as Br and NO_2 are valuable precursors and can be further transformed to other moieties, which may have promising applications in functional materials. For 2,2,4-trimethyl-1,3-pentanediol (**1h**), a fullerene-fused tetrahydrofuran **3** was also obtained besides the expected fullerene-fused dioxepane **2h** under the optimized conditions. Interestingly, compound **3** could be formed in 33% isolated yield as a predominant product when the amount of **1h** was increased from 5 to 20 equiv (Scheme 1). Additionally, product **2h** could also be selectively produced in 20% yield by decreasing the reaction temperature from 100 to 80 °C together with changing the reaction solvent from ODCB/CH_3CN to ODCB (Scheme 1). It should be pointed out that the formation of fullerene-fused tetrahydrofuran **3** was probably attributed to the cleavage of the carbon−carbon bond between C2 and C3 of **1h**, and the addition of CH_3CN further accelerated the cleavage process

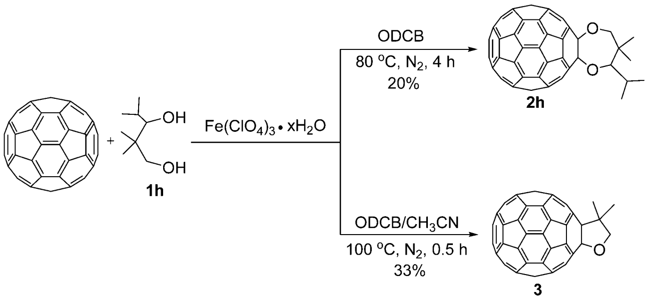
Table 2. Reaction Conditions and Yields for the Reaction of C_{60} with Diols 1a−m in the Presence of $Fe(ClO_4)_3$[a]



diol **1**	time (h)	yield (%) of **2**[b]
 **1a**	24	21 (88)
 **1b**	24[c]	22 (96)
 **1c**	24[c]	25 (86)
 **1d**	17	29 (71)
 **1e**	24	22 (96)
 **1f**	23	30 (97)
 **1g**	17	28 (70)
 **1h**	4[d]	20 (71)
 **1i**	7	34 (72)
 **1j**	24	0
 **1k**	24	trace
 **1l**	24	trace
 **1m**	24	0

[a]All reactions were performed in *o*-dichlorobenzene (6 mL) and acetonitrile (2 mL) under nitrogen conditions at 100 °C unless otherwise indicated; molar ratio refers to $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/\mathbf{1}$ = 1:2:5. [b]Isolated yield; those in parentheses were based on consumed C_{60}. [c]Molar ratio of $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/\mathbf{1b}$ or **1c** = 1:2:10. [d]The reaction of C_{60} with **1h** was conducted in *o*-dichlorobenzene (6 mL) at 80 °C.

Scheme 1. Reaction of C_{60} with 2,2,4-Trimethyl-1,3-pentanediol 1h Promoted by $Fe(ClO_4)_3$, Affording Fullerene-Fused Dioxepane 2h and Fullerene-Fused Tetrahydrofuran 3



(see Supporting Information). In addition, other diols such as **1j**, **1k**, **1l**, and **1m** were also treated with C_{60} and $Fe(ClO_4)_3$ under standard conditions. Compound **1j** could not produce the anticipated fullerene-fused dioxepane **2j**, probably due to the easy oxidation of the phenolic hydroxyl group from **1j** in the presence of $Fe(ClO_4)_3$. As with **1k**, **1l**, and **1m**, only a trace amount or no yield of fullerene-fused dioxygenated ring compounds[13] was observed even by the addition of ligands/metal-chelating agents such as 2,2′-bipyridine and 18-crown-6, which was probably attributed to the difficulty in forming fullerene-fused large-sized cyclic structures.

To expand the scope of the reaction, triethylene glycol (**1n**), diethylene glycol (**1o**), and tripropylene glycol (**1p**) were also chosen to react with C_{60} in the presence of $Fe(ClO_4)_3$. Initially, we investigated the reaction of C_{60} with **1n** under standard conditions, that is, in a molar ratio of 1:2:5 ($C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/\mathbf{1n}$) in ODCB/$CH_3CN$ at 100 °C under the protection of nitrogen, and found that only a trace amount of fullerene-fused dioxane **2a** rather than the anticipated fullerene-fused crown ether was unexpectedly obtained even by prolonging the reaction time to 38 h (entry 1, Table 3). The yield of fullerene-fused dioxane **2a** could be increased to 12% when the reaction was conducted in ODCB instead of ODCB/CH_3CN for 29 h (entry 2, Table 3). We conjectured that the formation of **2a** should undergo the cleavage of a carbon−oxygen ether bond of triethylene glycol with the aid of $Fe(ClO_4)_3$. To obtain fullerene-fused crown ether, some ligands/metal-chelating agents such as triphenylphosphine (PPh_3), ethylenediaminetetraacetic acid (EDTA), 2,2′-bipyridine, and 18-crown-6 were added to the above-mentioned reaction system to decrease the $Fe(ClO_4)_3$-promoted cleavage of the carbon−oxygen ether bond. Unfortunately, the reaction of C_{60}, $Fe(ClO_4)_3$, and **1n** in ODCB in the presence of a given ligand/metal-chelating agent still could not produce the desired fullerene-fused crown ether, although the yield of fullerene-fused dioxane **2a** was remarkably decreased or vanished in some cases (entries 3−5, Table 3). As for 18-crown-6, a slightly increasing yield of fullerene-fused dioxane **2a** was observed (entry 6 vs entry 2, Table 3), which was probably due to the partial cleavage of the carbon−oxygen ether bond from 18-crown-6 in the presence of $Fe(ClO_4)_3$ (entry 7, Table 3). Increasing the amount of **1n** and increasing the reaction temperature in the absence of ligands/metal-chelating agents could improve the yield of **2a** (entries 8 and 9, Table 3). To obtain an acceptable yield of **2a**, the reaction of C_{60}, $Fe(ClO_4)_3$, and **1n** was further conducted in a molar ratio of 1:5:20 in ODCB at 150 °C for 0.5 h and was found to give 24% yield of **2a** (entry 10, Table 3). Accordingly, the reaction conditions listed in entry 10 were chosen as the optimized conditions.

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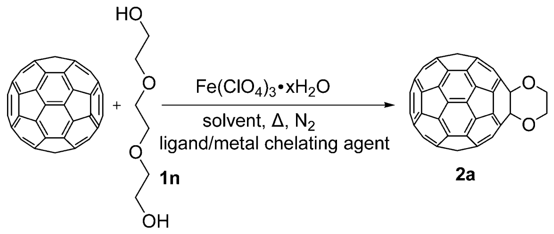
Table 3. Optimization of Reaction Conditions for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Triethylene Glycol 1n[a]

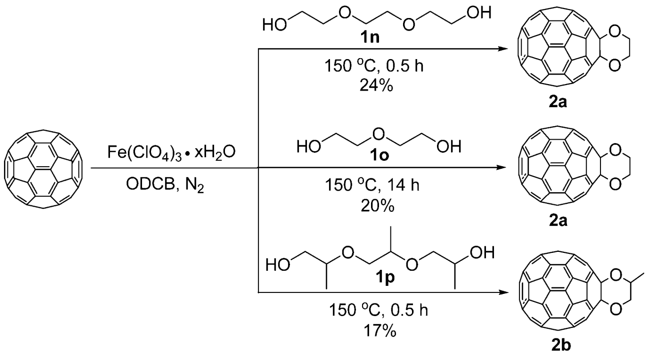


entry	ligand/metal-chelating agent	molar ratio[b]	solvent	temp (°C)	time (h)	yield (%) of **2a**[c]
1	none	1:2:5:0	ODCB/CH_3CN	100	38	trace
2	none	1:2:5:0	ODCB	100	29	12 (92)
3	PPh_3	1:2:5:2	ODCB	100	24	5 (45)
4	EDTA	1:2:5:2	ODCB	100	24	0
5	2,2′-bipyridine	1:2:5:2	ODCB	100	24	0
6	18-crown-6	1:2:5:2	ODCB	100	24	14 (26)
7	18-crown-6	1:2:0:2	ODCB	100	2	trace
8	none	1:2:20:0	ODCB	100	24	15 (83)
9	none	1:2:5:0	ODCB	130	24	15 (47)
10	**none**	**1:5:20:0**	**ODCB**	**150**	**0.5**	**24 (75)**

[a] All reactions were performed under nitrogen conditions unless otherwise indicated. [b] Molar ratio refers to C_{60}/$Fe(ClO_4)_3$·xH_2O/**1n**/ligand or metal-chelating agent. [c] Isolated yield; those in parentheses were based on consumed C_{60}.

Similar treatment of C_{60} with **1o** and **1p** in the presence of $Fe(ClO_4)_3$ under the optimized conditions also afforded the unexpected fullerene-fused dioxane derivatives **2a** and **2b** in 20% and 17% yield, respectively (Scheme 2). Therefore, the reaction of C_{60} with triethylene glycol, diethylene glycol, and tripropylene glycol provided the second route to fullerene-fused dioxanes.

Scheme 2. Reaction of C_{60} with Triethylene Glycol, Diethylene Glycol, and Tripropylene Glycol in the Presence of $Fe(ClO_4)_3$

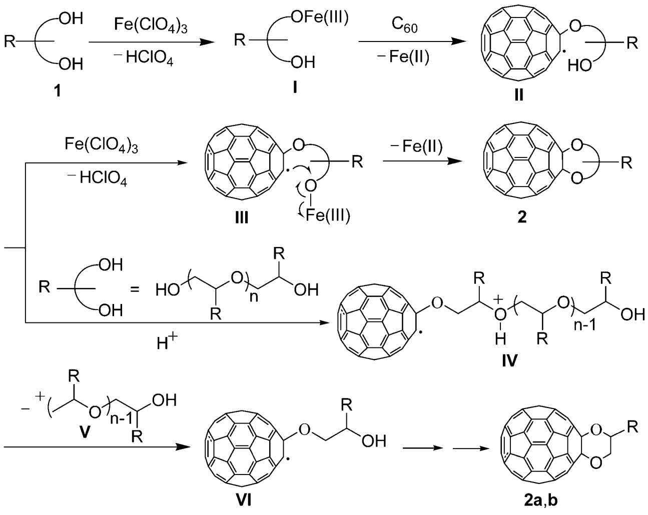


Fullerene-fused dioxane/dioxepane derivatives **2a**,[3] **2d**,[3] and **2e**[3] are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature. Fullerene-fused dioxanes/dioxepanes **2b**, **2c**, and **2f–i** are new compounds, and their structures were unambiguously established by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV–vis spectra. All high-resolution mass spectra of these new products gave the correct molecular ion peaks. Their IR spectra showed strong absorptions at 1062–1088 cm^{-1} due to the C–O group. Their UV–vis spectra exhibited a peak at 418–422 nm, which is a diagnostic absorption for the 1,2-adduct of C_{60}. In their ^{1}H NMR spectra, products **2b**, **2c**, **2h**, and **2i** displayed the expected chemical shifts as well as the splitting patterns for all protons. Nevertheless, compounds **2f** and **2g** gave the unexpected chemical shifts together with splitting patterns; that is, the methylene protons of **2f** or **2g** as well as the methyl protons of **2g** were non-equivalent and thus exhibited four signals, including three broad peaks for **2f** together with four broad peaks for **2g**. The reason for this phenomenon was probably due to a gauche conformational effect of the seven-membered ring.[14] In their ^{13}C NMR spectra, compounds **2b** and **2h** showed similar spectral patterns, and there were at least 31 peaks, including some overlapped ones due to the 58 sp^2-carbons of the fullerene moiety, consistent with the C_1 symmetry of the molecular structures; the peaks for the two sp^3-carbons of the C_{60} cage appeared at 87.15–91.90 and 86.28–91.65 ppm. However, products **2c** and **2i** exhibited different spectral patterns with the above-mentioned **2b** and **2h**. The observation of no more than 27 signals for the sp^2-carbons of the C_{60} skeleton agreed well with the C_s molecular symmetry, and the two sp^3-carbons were located at 86.63–91.49 ppm. For products **2f** and **2g**, the two sp^3-carbons of the C_{60} skeleton appeared at 91.41–92.30 ppm, yet the methyl carbons on the heterocyclic ring and the eight sp^2-carbons of the C_{60} moiety were not clearly observed. The exact reason for the disappearance of some carbon signals of **2f** and **2g** is not quite clear now. In addition, the structure of fullerene-fused tetrahydrofuran **3** was also fully characterized. Its MALDI-TOF MS showed the correct [M]$^+$ peak at m/z 792.0574. Its ^{1}H NMR spectrum displayed two singlets at 4.65 and 1.97 ppm for the two methylene protons and the six methyl protons. In its ^{13}C NMR spectrum, there were 26 peaks, including some overlapped ones in the 135–154 ppm range for the 58 sp^2-carbons of the C_{60} skeleton and two peaks at 98.56 and 74.96 ppm for the two sp^3-carbons of the C_{60} moiety, agreeing with its C_s symmetry. Its IR spectrum also showed the corresponding absorption at 1036 cm^{-1} which was due to the C–O group. Its UV–vis spectrum exhibited a characteristic absorption peak of the 1,2-adduct of C_{60} at 428 nm.

On the basis of the previously suggested mechanism for the fullerenyl boronic ester formation from the $Fe(ClO_4)_3$-mediated reaction of C_{60} with boronic acids,[3] the proposed mechanism for the formation of fullerene-fused dioxanes/

dioxepanes **2** from C_{60} and diols **1** in the presence of $Fe(ClO_4)_3$ is shown in Scheme 3. A chosen diol reacts with $Fe(ClO_4)_3$ to generate Fe(III) complex **I**, accompanied by the elimination of $HClO_4$. Addition of complex **I** to C_{60} produces fullerenyl radical **II**, which can undergo coordination with another molecule of $Fe(ClO_4)_3$ to form Fe(III) complex **III**, followed by intramolecular cyclization with the loss of an Fe(II) species to afford fullerene-fused dioxanes/dioxepanes **2**. For the reaction of C_{60} with diethylene glycol, triethylene glycol, and tripropylene glycol, the first two steps are the same as those for fullerene-fused dioxanes/dioxepanes **2** to generate fullerene radical **II**, which can undergo protonation of the oxygen atom from the ether group to form fullerene radical cation **IV**. Loss of carbocation **V** from radical cation **IV** leads to the formation of fullerene radical **VI**. The subsequent reactions of radical **VI** with C_{60} to produce fullerene-fused dioxanes **2a**,**b** are the same as those shown in Scheme 3. Alternatively, fullerenyl radicals **II** and **VI** could be oxidized to the corresponding fullerenyl cation, and subsequent cyclization with the loss of H^+ gave fullerene-fused dioxanes/dioxepanes **2**.

Scheme 3. Proposed Reaction Mechanism for the Formation of Fullerene-Fused Dioxanes/Dioxepanes



CONCLUSION

In summary, two routes to the rare fullerene-fused dioxanes/dioxepanes have been developed via the $Fe(ClO_4)_3$-mediated reaction of C_{60} with diols. The current one-step approach to the preparation of fullerene-fused dioxanes/dioxepanes was obviously more straightforward and practical than the previously reported protocol.[3] In addition, the reaction of C_{60} with 2,2,4-trimethyl-1,3-pentanediol in the presence of $Fe(ClO_4)_3$ in ODCB/CH_3CN selectively afforded the unexpected fullerene-fused tetrahydrofuran derivative, which would be difficult to prepare by other methods. A possible reaction mechanism for the formation of fullerene-fused dioxanes/dioxepanes is proposed.

EXPERIMENTAL SECTION

General Methods. ^1H NMR spectra were referenced to tetramethylsilane at 0.00 ppm, and ^{13}C NMR spectra were referenced to residual $CHCl_3$ at 77.16 ppm or DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode.

General Procedure for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Diols 1a–m. C_{60} (36.0 mg, 0.05 mmol) and a given amount of diol **1** (0.25 mmol, 0.50 mmol for **1b** and **1c**) were mixed in a 50 mL three-neck flask, which was equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. After the compounds were completely dissolved in 6 mL of ODCB by sonication, the resulting solution was deoxygenated with nitrogen for 10 min. After $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.10 mmol), dissolved in 2 mL of CH_3CN, was added, the reaction mixture was vigorously stirred in the oil bath preset at 100 °C under nitrogen atmosphere. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The resulting solution was passed through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent. Fullerene-fused dioxygenated ring compounds **2** were obtained along with unreacted C_{60}.

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Ethylene Glycol 1a under Different Conditions. A 50 mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol) and **1a** (0.10–0.40 mmol). After the added compounds were completely dissolved in ODCB (6 mL) by sonication, metal oxidant (0.05–0.15 mmol) dissolved in 2 mL of CH_3CN, DMSO, or DMF was added. The resulting solution was deoxygenated with nitrogen for 10 min, and then the mixture was heated with stirring in an oil bath preset at 80–120 °C under nitrogen atmosphere for a designated time (5–24 h, monitored by TLC). The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and C_{60}-fused dioxane **2a**.[3]

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Ethylene Glycol 1a on a Larger Scale. According to the general procedure, the reaction of C_{60} (216.0 mg, 0.30 mmol, dissolved in 36 mL of ODCB) with ethylene glycol **1a** (84 μL, 1.50 mmol, dissolved in 36 mL of ODCB) and $Fe(ClO_4)_3{\cdot}xH_2O$ (276.0 mg, 0.60 mmol, dissolved in 12 mL of CH_3CN) for 24 h in a 100 mL three-neck flask afforded first unreacted C_{60} (155.1 mg, 72%) and then **2a**[3] (42.1 mg, 18%) as an amorphous black solid.

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Ethylene Glycol 1a in the ODCB without the Addition of CH_3CN, DMSO, or DMF. A 50 mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.10 mmol), and ethylene glycol **1a** (14 μL, 0.25 mmol). After being completely dissolved in ODCB (6 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 100 °C under nitrogen atmosphere for 24 h. The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give first unreacted C_{60} (15.5 mg, 43%) and then C_{60}-fused dioxane **2a**[3] (6.7 mg, 17%).

Fullerene-Fused Dioxane 2a. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (14 μL, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.10 mmol) for 24 h afforded first unreacted C_{60} (27.4 mg, 76%) and then **2a**[3] (8.1 mg, 21%) as an amorphous black solid.

Fullerene-Fused Dioxane 2b. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (37 μL, 0.50 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.10 mmol) for 24 h afforded first unreacted C_{60} (27.8 mg, 77%) and then **2b** (8.6 mg, 22%) as an amorphous black solid: mp >300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 5.30–5.22 (m, 1H), 5.11 (dd, J = 11.1, 6.9 Hz, 1H), 4.45 (dd, J = 10.7, 6.0 Hz, 1H), 1.88 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) (all 1C unless indicated) δ 149.07, 148.94, 148.66, 148.44 (2C), 148.33, 146.49 (2C), 146.47 (2C), 146.17 (6C), 146.08 (2C), 145.65, 145.46, 145.44, 145.35, 145.25 (3C), 145.13, 145.10 (2C), 144.74 (3C), 144.68, 142.60 (2C), 142.55 (4C), 142.22 (4C), 141.77 (3C), 141.62 (3C), 141.09, 141.00, 139.58 (2C), 135.51

(2C), 138.49, 138.04, 137.05, 136.99, 87.15 (sp^3-*C* of C_{60}), 86.28 (sp^3-*C* of C_{60}), 67.80, 22.17; FT-IR ν/cm^{-1} (KBr) 2921, 2860, 1424, 1375, 1178, 1154, 1126, 1062, 993, 575, 526; UV−vis (CHCl$_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{63}H_6O_2$ [M]$^+$ 794.0368, found 794.0365.

Fullerene-Fused Dioxane 2c. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (45 μL, 0.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 24 h afforded first unreacted C_{60} (25.6 mg, 71%) and then **2c** (10.0 mg, 25%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$) δ 5.44−5.37 (m, 2H), δ 1.79 (d, *J* = 5.7, 6H); ^{13}C NMR (100 MHz, CS$_2$/DMSO-*d*$_6$) (all 2C unless indicated) δ 148.67, 148.44, 147.67, 145.74, 145.72, 145.41, 145.39, 145.35 (4C), 144.91, 144.76 (1C), 144.62, 144.52 (3C), 144.33, 144.02 (4C), 141.87, 141.82 (4C), 141.48 (4C), 141.07, 141.01, 140.89, 140.34, 138.82, 138.74, 137.63, 136.13, 86.63 (sp^3-*C* of C_{60}), 70.51, 16.53; FT-IR ν/cm^{-1} (KBr) 2981, 2892, 1463, 1430, 1379, 1187, 1129, 1076, 1054, 1038, 897, 526; UV−vis (CHCl$_3$) λ_{max}/nm 258, 318, 419; MALDI-TOF MS *m*/*z* calcd for $C_{64}H_8O_2$ [M]$^+$ 808.0524, found 808.0520.

Fullerene-Fused Dioxepane 2d. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (18 μL, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 17 h afforded first unreacted C_{60} (21.4 mg, 59%) and then **2d**[3] (11.6 mg, 29%) as an amorphous black solid.

Fullerene-Fused Dioxepane 2e. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (22 μL, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 24 h afforded first unreacted C_{60} (27.7 mg, 77%) and then **2e**[3] (8.7 mg, 22%) as an amorphous black solid.

Fullerene-Fused Dioxepane 2f. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (22 μL, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 23 h afforded first unreacted C_{60} (25.0 mg, 69%) and then **2f** (12.0 mg, 30%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/DMSO-*d*$_6$) δ 4.78 (br s, 2H), 4.66 (t, *J* = 10.0 Hz, 2H), 2.88 (br s, 1H), 1.21 (br s, 3H); ^{13}C NMR (100 MHz, CS$_2$/DMSO-*d*$_6$) (all 2C unless indicated) δ 150.66 (4C, weak), 147.83, 145.82 (4C), 145.42 (4C), 145.31, 145.20, 144.69, 144.59 (4C), 144.48, 144.31, 144.09, 144.00, 141.85 (6C), 141.62 (4C), 140.87, 140.72, 138.67, 138.58, 91.41 (sp^3-*C* of C_{60}), 76.12, 35.56 (1C); FT-IR ν/cm^{-1} (KBr) 2924, 2861, 1510, 1457, 1430, 1389, 1357, 1216, 1168, 1124, 1088, 1024, 977, 908, 599, 526; UV−vis (CHCl$_3$) λ_{max}/nm 258, 318, 422; MALDI-TOF MS *m*/*z* calcd for $C_{64}H_8O_2$ [M]$^+$ 808.0524, found 808.0521.

Fullerene-Fused Dioxepane 2g. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (26.0 mg, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 17 h afforded first unreacted C_{60} (21.6 mg, 60%) and then **2g** (11.5 mg, 28%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/DMSO-*d*$_6$) δ 4.88 (br s, 2H), 4.28 (br s, 2H), 1.80 (br s, 3H), 1.16 (br s, 3H); ^{13}C NMR (100 MHz, CS$_2$/CDCl$_3$) (all 4C unless indicated) δ 151.55 (weak), 148.54 (2C), 146.52, 146.12, 145.96, 145.25 (6C), 145.20, 144.70, 142.52 (6C), 142.28, 141.58 (weak), 139.31, 92.30 (2C, sp^3-*C* of C_{60}), 80.75 (2C), 36.71 (1C); FT-IR ν/cm^{-1} (KBr) 2917, 2847, 1513, 1461, 1432, 1358, 1180, 1124, 1083, 979, 901, 574, 525; UV−vis (CHCl$_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{65}H_{10}O_2$ [M]$^+$ 822.0681, found 822.0680.

Fullerene-Fused Dioxepane 2h. By following the same experimental procedure as for the $Fe(ClO_4)_3 \cdot xH_2O$-mediated reaction of C_{60} with ethylene glycol **1a** in the ODCB, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (37 mg, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) at 80 °C for 4 h afforded first unreacted C_{60} (26.0 mg, 72%) and then **2h** (8.5 mg, 20%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$) δ 4.92 (d, *J* = 12.6 Hz, 1H), 4.66 (s, 1H), 4.20 (d, *J* = 12.6 Hz, 1H), 2.33−2.29 (m, 1H), 1.77 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CS$_2$/CDCl$_3$) (all 1C unless indicated) δ 152.08, 151.36, 149.72, 149.36, 148.52 (2C), 146.49 (2C), 146.46 (2C), 146.12 (4C), 146.00, 145.94 (2C), 145.77, 145.74, 145.47, 145.43, 145.34 (2C), 145.15, 145.07, 145.04, 144.86 (2C), 144.73, 144.66, 144.56, 144.52, 142.52 (4C), 142.47 (2C), 142.25 (4C), 142.04, 142.00, 141.72, 141.64, 141.36, 141.27, 140.77 (2C), 139.40, 139.33, 139.28, 139.16, 138.78 (2C), 136.37, 135.82, 91.90 (sp^3-*C* of C_{60}), 91.65 (sp^3-*C* of C_{60}), 83.42, 39.96, 29.87, 23.91, 22.21, 19.97, 18.40; FT-IR ν/cm^{-1} (KBr) 2924, 2864, 1463, 1431, 1392, 1364, 1217, 1179, 1124, 1078, 1046, 989, 575, 526; UV−vis (CHCl$_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{68}H_{16}O_2$ [M]$^+$ 864.1150, found 864.1152.

Fullerene-Fused Dioxepane 2i. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (50.0 mg, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) at 100 °C for 7 h afforded first unreacted C_{60} (19.0 mg, 53%) and then **2i** (15.6 mg, 34%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/DMSO-*d*$_6$) δ 5.67 (d, *J* = 11.4 Hz, 2H), 5.51 (d, *J* = 11.4 Hz, 2H); ^{13}C NMR (100 MHz, CS$_2$/DMSO-*d*$_6$) (all 2C unless indicated) δ 148.94 (4C), 147.91, 145.91 (4C), 145.65 (1C), 145.58 (4C), 145.48 (1C), 145.29, 144.74, 144.59 (1C), 144.53, 144.44, 144.34 (1C), 144.07, 143.81, 143.54, 141.92 (3C), 141.88 (3C), 141.62, 141.59, 141.14, 141.07, 140.73, 139.85, 138.90, 138.77, 138.67, 135.52, 91.49 (sp^3-*C* of C_{60}), 83.87 (1C), 73.40; FT-IR ν/cm^{-1} (KBr) 2915, 2844, 1562, 1511, 1461, 1429, 1338, 1181, 1127, 1082, 979, 898, 839, 735, 599, 564, 526; UV−vis (CHCl$_3$) λ_{max}/nm 257, 319, 418; MALDI-TOF MS *m*/*z* calcd for $C_{63}H_4BrNO_4$ [M]$^+$ 916.9324, found 916.9322.

Fullerene-Fused Tetrahydrofuran 3. According to the general procedure for the preparation of fullerene-fused dioxanes/dioxepanes **2a**−**g** and **2i**, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (146.0 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) at 100 °C for 0.5 h afforded first unreacted C_{60} (23.0 mg, 64%) and then **3** (13.1 mg, 33%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/DMSO-*d*$_6$) δ 4.65 (s, 2H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, CS$_2$/DMSO-*d*$_6$) (all 2C unless indicated) δ 153.28, 149.24, 147.14 (1C), 146.52 (1C), 145.54, 145.37, 145.29, 145.22, 145.10, 144.96, 144.64, 144.54, 144.34 (4C), 144.23, 143.74 (4C), 142.10, 141.85, 141.82, 141.41 (4C), 141.37 (4C), 141.09, 140.81, 139.01, 138.89, 137.16, 135.96, 98.56 (1C, sp^3-*C* of C_{60}), 77.36 (1C), 74.96 (1C, sp^3-*C* of C_{60}), 50.59 (1C), 25.28; FT-IR ν/cm^{-1} (KBr) 2924, 2837, 1461, 1428, 1387, 1368, 1229, 1179, 1102, 1036, 990, 965, 952, 899, 563, 553, 526; UV−vis (CHCl$_3$) λ_{max}/nm 257, 316, 428; MALDI-TOF MS *m*/*z* calcd for $C_{64}H_8O$ [M]$^+$ 792.0575, found 792.0574.

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Triethylene Glycol 1n. By following the same experimental procedure as for the $Fe(ClO_4)_3 \cdot xH_2O$-mediated reaction of C_{60} with ethylene glycol **1a** in the ODCB, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1n** (132 μL, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) at 150 °C for 0.5 h afforded first unreacted C_{60} (24.6 mg, 68%) and then fullerene-fused dioxane **2a**[3] (9.5 mg, 24%) as an amorphous black solid.

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Diethylene Glycol 1o. By following the same experimental procedure as for the $Fe(ClO_4)_3 \cdot xH_2O$-mediated reaction of C_{60} with ethylene glycol **1a** in the ODCB, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1o** (95 μL, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) at 150 °C for 14 h afforded first unreacted C_{60} (26.1 mg, 73%) and then fullerene-fused dioxane **2a**[3] (7.7 mg, 20%) as an amorphous black solid.

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Tripropylene Glycol 1p. By following the same experimental procedure as for the $Fe(ClO_4)_3 \cdot xH_2O$-mediated reaction of C_{60} with ethylene glycol **1a** in the ODCB, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1p** (188 μL, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) at 150 °C for 0.5 h afforded first unreacted C_{60} (16.9 mg, 47%) and then fullerene-fused dioxane **2b** (6.6 mg, 17%) as an amorphous black solid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

HPLC and NMR spectra of products **2a**−**i**, and **3**, UV−vis spectra of **2b**, **2f**, and **3**, as well as HRMS of **2b**, **2g**, and **3**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00360.

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Notes

The authors declare no competing financial interest.

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