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A Facile Access to [60]Fullerene-Fused 1,3-Dioxolanes: Reaction of [60]Fullerene with Aldehydes/Ketones Promoted by Ferric Perchlorate

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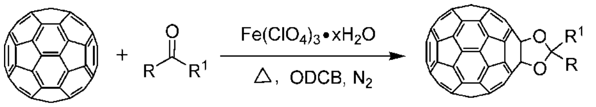
ABSTRACT



21 examples, 9-38% yield
(24-91% based on converted C_{60})

The facile reaction of [60]fullerene (C_{60}) with various aldehydes or ketones in the presence of ferric perchlorate successfully afforded the rare C_{60}-fused 1,3-dioxolanes. A possible reaction mechanism for the formation of the C_{60}-fused 1,3-dioxolanes is proposed.

Since the availability of fullerenes in a macroscopic amount, various types of reactions for the functionalization of fullerenes have been discovered, and numerous fullerene products with wide structural diversities have been prepared.[1] However, fullerene-fused 1,3-dioxolane derivatives[2−4] have been relatively rare until now. Elemes et al. reported the synthesis of the first fullerene-fused 1,3-dioxolane as one of the two products via the reaction of [60]fullerene (C_{60}) with dimethyldioxirane.[2a] Wang et al. described the preparation of another C_{60}-fused 1,3-dioxolane by the reaction of C_{60} with $PhCH_2ONa$-$PhCH_2OH$ under aerobic conditions.[2b] It should be noted that the latter methodology was only limited to benzoxide as the reaction of C_{60} with other alkoxides gave fullerene products with a C_{60}-fused tetrahydrofuran ring skeleton and an acetal moiety.[5] The research groups of Tajima[3a] and Gan[3b] realized the synthesis of C_{60}-fused 1,3-dioxolane derivatives from fullerene epoxides through the reactions with aldehydes or acetone in the presence of a Lewis acid. Two orthoester-type 1,3-dioxolanofullerenes were also reported.[4] Among the reported C_{60}-fused 1,3-dioxolane derivatives, only four were prepared directly from C_{60}.[2,4] Therefore, it is still demanding to develop new protocol to obtain C_{60}-fused 1,3-dioxolane derivatives directly from C_{60} in a straightforward and efficient way with a broad substrate scope.

Recently, our group has been interested in reactions of C_{60} mediated by metal salts such as $Mn(OAc)_3$,[6,7] $Cu(OAc)_2$,[7c] $Pb(OAc)_4$,[7h] or $Pd(OAc)_2$[8] to prepare a series

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(1) For selected reviews, see: (a) Hirsch, A. *Synthesis* **1995**, 895. (b) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049. For some recent papers, see: (c) Zhang, G.; Huang, S.; Xiao, Z.; Chen, Q.; Gan, L.; Wang, Z. *J. Am. Chem. Soc.* **2008**, *130*, 12614. (d) Murata, M.; Maeda, S.; Morinaka, Y.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2008**, *130*, 15800. (e) Filippone, S.; Maroto, E. E.; Martin-Domenech, A.; Suarez, M.; Martin, N. *Nat. Chem.* **2009**, *1*, 578. (f) Clavaguera, S.; Khan, S. I.; Rubin, Y. *Org. Lett.* **2009**, *11*, 1389. (g) Wang, G.-W.; Lu, Y.-M.; Chen, Z.-X. *Org. Lett.* **2009**, *11*, 1507. (h) Tzirakis, M. D.; Orfanopoulos, M. *J. Am. Chem. Soc.* **2009**, *131*, 4063. (i) Li, C. Z.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 17058.

(2) (a) Elemes, Y.; Silverman, S. K.; Sheu, C. M.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351. (b) Wang, G.-W.; Shu, L.-H.; Wu, S.-H.; Wu, H.-M.; Lao, X.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1071.

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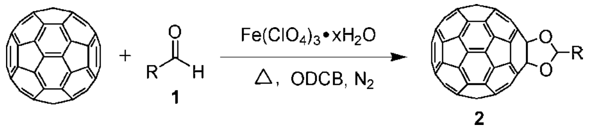
of novel fullerene derivatives. We also reported the synthesis of rare fullerooxazoles by the $Fe(ClO_4)_3$-mediated reaction of C_{60} with a variety of nitriles,[9] which is the first example for the direct reaction of C_{60} with the unsaturated carbon−nitrogen triple bond moiety of nitriles in the presence of water. In continuation of our interest in $Fe(ClO_4)_3$-mediated reactions of C_{60},[9] herein we describe the $Fe(ClO_4)_3$-mediated one-step reaction of C_{60} with aldehydes or ketones to afford a variety of scarce C_{60}-fused 1,3-dioxolane derivatives.

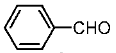
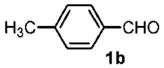
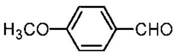
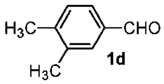
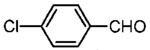
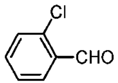
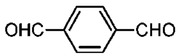
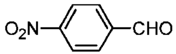
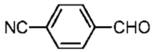
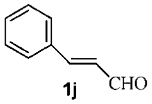
In our previous study, we found that the direct dissolution[10] of $Fe(ClO_4)_3$ by nitriles played a crucial role for the successful synthesis of fullerooxazoles.[9] Similarly, we explored the $Fe(ClO_4)_3$-promoted reaction of C_{60} with various aldehydes by adopting the direct dissolution method, i.e., $Fe(ClO_4)_3$ was first dissolved in a chosen aldehyde, and then the dichlorobenzene (ODCB) solution of C_{60} was added. Much to our satisfaction, we found that the $Fe(ClO_4)_3$-mediated reaction of C_{60} with aldehydes **1a**−**k**, that is, benzaldehyde (**1a**), *p*-tolualdehyde (**1b**), 4-methoxybenzaldehyde (**1c**), 3,4-dimethylbenzaldehyde (**1d**), 4-chlorobenzaldehyde (**1e**), 2-chlorobenzaldehyde (**1f**), *p*-phthalaldehyde (**1g**), 4-nitrobenzaldehyde (**1h**), 4-cyanobenzaldehyde (**1i**), cinnamaldehyde (**1j**), and propionaldehyde (**1k**), afforded C_{60}-fused 1,3-dioxolane derivatives **2a**−**k**.

Initially, the $Fe(ClO_4)_3$-promoted reaction of C_{60} with **1a** was chosen to screen the reaction conditions. The details are listed in Table S1 in the Supporting Information. Screening experiments indicated that the best molar ratio of C_{60}:$Fe(ClO_4)_3 \cdot xH_2O$:**1a** was 1:2:5, and the reaction temperature was 80 °C. These optimized reaction conditions could be extended to other aldehydes except that higher temperature was required for the melting of **1g**−**i** and subsequent dissolution of $Fe(ClO_4)_3$, and more propionaldehyde was demanded due to its lower boiling point and thus easier evaporation. The reaction conditions and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with aldehydes **1a**−**k** are summarized in Table 1. The progress of the reactions should be carefully monitored by TLC to prevent overreaction.

As can be seen from Table 1, aromatic aldehydes bearing either electron-donating or electron-withdrawing groups (**1a**−**i**), cinnamaldehyde (**1j**), as well as aliphatic aldehyde (**1k**) could be successfully employed to prepare the C_{60}-fused 1,3-dioxolane derivatives in 14−38% yields (30−91% based on consumed C_{60}). For the synthesis of compound **2a**, the current $Fe(ClO_4)_3$-mediated reaction of C_{60} with benzaldehyde is preferable to the reaction of C_{60} with $PhCH_2ONa$-$PhCH_2OH$, which generated product **2a** in 15% yield (68% based on consumed C_{60}).[2b] The cyano group is known to react with C_{60} in the presence of $Fe(ClO_4)_3$.[9] Nevertheless, no corresponding fullerooxazole could be identified from the $Fe(ClO_4)_3$-mediated reaction of C_{60} with substrate **1i**, demonstrating the superior reactivity of the aldehyde group over the cyano group.

Table 1. Reaction Conditions and Yields for the Reaction of C_{60} with Aldehydes **1a**−**k** in the Presence of $Fe(ClO_4)_3 \cdot xH_2O$[a]



aldehyde 1	reaction temp (°C)	reaction time (min)	yield of **2** (%)[c]
 **1a**	80	100	34 (85)
 **1b**	80	70	28 (90)
 **1c**	80	70	29 (88)
 **1d**	80	40	38 (91)
 **1e**	80	50	31 (91)
 **1f**	80	150	32 (76)
 **1g**	120	30	18 (47)
 **1h**	120	35	19 (30)
 **1i**	120	90	23 (77)
 **1j**	80	35	30 (81)
CH_3CH_2CHO **1k**	80[b]	150	14 (52)

[a] All reactions were performed under protection of nitrogen with a molar ratio of C_{60}:$Fe(ClO_4)_3 \cdot xH_2O$:**1** = 1:2:5 unless otherwise indicated. [b] Molar ratio of C_{60}:$Fe(ClO_4)_3 \cdot xH_2O$:**1k** = 1:2:50. [c] Isolated yield; the number in parentheses was based on consumed C_{60}.

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(5) Wang, G.-W.; Lu, Y.-M.; Chen, Z.-X.; Wu, S.-H. *J. Org. Chem.* **2009**, *74*, 4841.

(6) For a review, see: Wang, G.-W.; Li, F.-B. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1162.

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(9) Li, F.-B.; Liu, T.-X.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 6417.

(10) The term “melting” in ref 9 should be better expressed as “dissolution”.

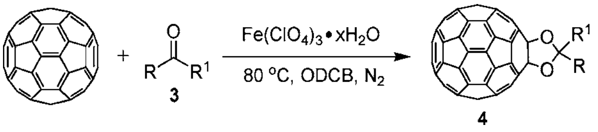
Product **2a**[2b,3a] is a known compound, and its identity was confirmed by comparison of its spectral data with those reported in the literature. New compounds **2b**−**k** were unambiguously characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In the ^{1}H NMR spectra of compounds **2b**−**k**, the methine proton on the heterocycle ring appeared in very downfield region (6.3−7.6 ppm). In their ^{13}C NMR spectra, the observation of no more than 30 lines for the sp^2-carbons of the C_{60} skeleton was consistent with their C_s molecular symmetry, and the signals for the sp^3-carbons of the acetal and fullerene moiety were located at 99.2−104.1 and 93.5−94.6 ppm, close to those of reported C_{60}-fused 1,3-dioxolane derivatives in the previous literature.[2,3]

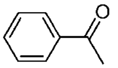
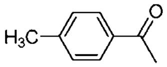
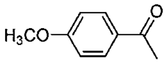
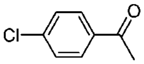
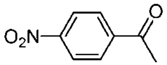
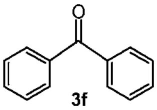
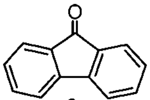
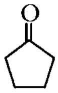
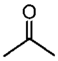
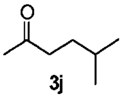
To expand the scope of the reaction, the substrates were extended from aldehydes to ketones. Acetophenone (**3a**), 4-methylacetophenone (**3b**), 4-methoxyacetophenone (**3c**), 4-chloroacetophenone (**3d**), 4-nitroacetophenone (**3e**), benzophenone (**3f**), 9-fluorenone (**3g**), cyclopentanone (**3h**), acetone (**3i**), and 5-methyl-2-hexanone (**3j**) were chosen to react with C_{60} in the presence of $Fe(ClO_4)_3$ by the direct dissolution method, and were found to generate C_{60}-fused 1,3-dioxolane derivatives **4a**−**j**.

The reaction conditions and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with ketones **3a**−**j** are summarized in Table 2.

As can be seen from Table 2, both aromatic ketones (**3a**−**g**) and aliphatic ketones (**3h**−**j**) could be successfully utilized to prepare the C_{60}-fused 1,3-dioxolane derivatives **4a**−**j** in 9−29% yields (24−68% based on consumed C_{60}). The acyclic aromatic ketones (**3a**−**f**) gave reasonably good isolated yields except 4-nitroacetophenone (**3e**), which afforded some byproducts. 9-Fluorenone also generated low yield probably due to the steric interactions from the two hydrogens at the C_1 and C_8 positions in the rigid ring system. Aliphatic ketones (**3h**−**j**) generally afforded good product yields. The isolated yield of C_{60}-fused 1,3-dioxolane derivative **4i** by our current protocol (18%, 44% based on consumed C_{60}) was much higher than that by the previously reported procedure (5%, 7% based on consumed C_{60}).[2a]

Table 2. Reaction Conditions and Yields for the Reaction of C_{60} with Ketones **3a**−**j** in the Presence of $Fe(ClO_4)_3{\cdot}xH_2O$[a]



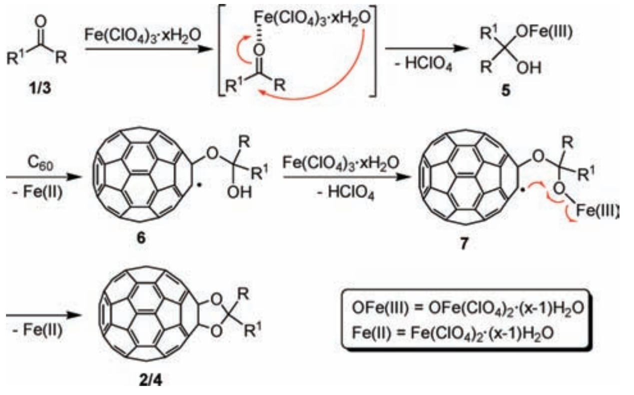
ketone **3**	molar ratio[b]	reaction time (min)	yield of **4** (%)[c]
 **3a**	1:2:5	35	19 (37)
 **3b**	1:2:5	45	20 (38)
 **3c**	1:2:5	70	17 (33)
 **3d**	1:2:5	35	27 (68)
 **3e**	1:2:20	90	9 (53)
 **3f**	1:2:5	90	21 (60)
 **3g**	1:2:50	45	12 (24)
 **3h**	1:2:5	45	29 (58)
 **3i**	1:2:50	140	18 (44)
 **3j**	1:2:5	40	28 (51)

[a] All reactions were performed at 80 °C under protection of nitrogen. [b] Molar ratio refers to C_{60}:$Fe(ClO_4)_3{\cdot}xH_2O$:**3**. [c] Isolated yield; the number in parentheses was based on consumed C_{60}.

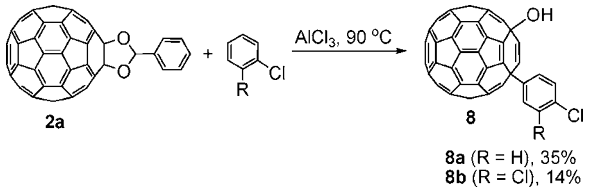
The structures of C_{60}-fused dioxolanes **4a**−**j** were fully established by HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In their ^{13}C NMR spectra, dioxolanes **4a**−**e** together with **4j** showed similar spectral patterns with those from aldehydes **1a**−**k**. No more than 29 peaks including some overlapped ones due to the 58 sp^2-carbons of the fullerene moiety were observed in the range of 137.3−149.4 ppm, consistent with the C_s symmetry of the molecular structures, and the peaks for the two sp^3-carbons of the C_{60} cage and ketal carbon appeared at 94.4−95.1 and 110.6−113.8 ppm. However, the remaining dioxolanes **4f**−**i** exhibited different spectral patterns with the above-mentioned dioxolanes. The observation of only 14−16 lines for the sp^2-carbons of the C_{60} skeleton agreed well with the C_{2v} molecular symmetry, and the two sp^3-carbons and ketal carbon were located at 93.5−95.6 and 111.7−120.7 ppm. Interestingly, the chemical shifts for the ketal carbons (110.6−120.7 ppm) in the dioxolanes **4a**−**j** were shifted downfield about 11−17 ppm from those of the acetal carbons in the dioxolanes **2b**−**k** (99.2−104.1 ppm). In addition, the identity of **4i** was further confirmed by comparison of its spectral data with those reported previously.[2a]

We previously reported that the reaction of methyl ketones with C_{60} promoted by $Mn(OAc)_3/Cu(OAc)_2$ gave C_{60}-fused dihydrofurans and/or methanofullerenes.[7c] However, no evidence for the formation of C_{60}-fused dihydrofuran and/

Scheme 1. Proposed Reaction Mechanism for the Formation of C_{60}-Fused 1,3-Dioxolanes



Scheme 2. Reaction of C_{60}-Fused Dioxolane **2a** with Chlorobenzene and 1,2-Dichlorobenzene in the Presence of Aluminum Chloride



or methanofullerene could be obtained from the current $Fe(ClO_4)_3$-mediated reaction of C_{60} with methyl ketones. Obviously, different reaction mechanisms are operating for the reaction of C_{60} with methyl ketones mediated by $Fe(ClO_4)_3$ and $Mn(OAc)_3/Cu(OAc)_2$. On the basis of the previously suggested mechanism for the reaction of C_{60} with various nitriles in the presence of $Fe(ClO_4)_3$ to afford the fullerooxazoles,[9] we propose a possible mechanism for the formation of C_{60}-fused 1,3-dioxolanes **2**/**4** from the $Fe(ClO_4)_3$-mediated reaction of C_{60} with aldehydes/ketones, as shown in Scheme 1. A chosen aldehyde or ketone reacts with the hydrated H_2O in $Fe(ClO_4)_3{\cdot}xH_2O$ to produce Fe(III)-complex **5** accompanied by the loss of $HClO_4$. The observed reddening of the mixtures of aldehydes/ketones and $Fe(ClO_4)_3{\cdot}xH_2O$ hints the formation of complexes between $Fe(ClO_4)_3{\cdot}xH_2O$ and aldehydes/ketones.[11] Homolytical addition of **5** to C_{60} generates fullerenyl radical **6** with an elimination of $Fe(ClO_4)_2{\cdot}(x\text{-}1)H_2O$, and then coordination with another molecule of $Fe(ClO_4)_3{\cdot}xH_2O$ to form Fe(III)-complex **7**, which undergoes intramolecular cyclization with the loss of a Fe(II) species to afford C_{60}-fused 1,3-dioxolanes **2**/**4**.

The C_{60}-fused 1,3-dioxolane derivatives can be valuable precursors for further functionalization. Preliminary results showed that treatment of C_{60}-fused 1,3-dioxolane derivative **2a** with $AlCl_3$ in chlorobenzene and 1,2-dichlorobenzene at 90 °C afforded 4-chlorophenyl- and 3,4-dichlorophenyl-substituted fullerenols in 35% and 14% yield, respectively (Scheme 2). Tajima et al.[12] reported the $BF_3{\cdot}Et_2O$-assisted nucleophilic substitution of $C_{60}O$. They found that the progress of the reaction depended considerably on the nucleophilicity of the aromatic compound, and chlorobenzene failed to react with $C_{60}O$. Even though the reaction mechanism for the formation of fullerenols **8** is not quite clear now, the reaction should occur via a carbocationic intermediate generated with the assistance of $AlCl_3$. It is intriguing that electron-deficient chlorobenzene and 1,2-dichlorobenzene could react in our case.

In summary, the synthesis of scarce C_{60}-fused 1,3-dioxolanes has been achieved by the $Fe(ClO_4)_3$-promoted reaction of C_{60} with aldehydes or ketones. It is noteworthy that functional groups such as Cl, CHO, NO_2, and CN could be tolerated under our reaction conditions and can be further transformed to other moieties. The current one-step approach to the preparation of C_{60}-fused 1,3-dioxolanes from cheap and easily accessible aldehydes/ketones and $Fe(ClO_4)_3$ was obviously more straightforward and practical than the previous protocols.[2,3a] The direct dissolution of aldehydes/ketones and $Fe(ClO_4)_3$ proved to be crucial for the efficient synthesis of C_{60}-fused 1,3-dioxolanes. A plausible reaction mechanism for the formation of C_{60}-fused 1,3-dioxolanes is suggested.

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Supporting Information Available: Experimental procedures, optimization results, and characterization data, as well as the ^{1}H NMR and ^{13}C NMR spectra of products **2a**−**k**, **4a**−**j**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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