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Synthesis of Fullerene-Fused Lactones and Fullerenyl Esters: Radical Reaction of [60]Fullerene with Carboxylic Acids Promoted by Manganese(III) Acetate and Lead(IV) Acetate

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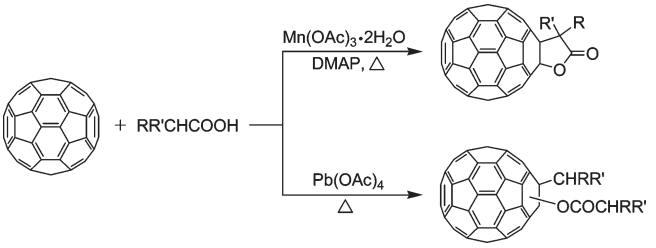

The manganese(III) acetate-mediated radical reaction of [60]fullerene with carboxylic acids in the presence of 4-(dimethylamino)pyridine exclusively afforded the [60]fullerene-fused lactones. Interestingly, the lead(IV) acetate-promoted radical reaction of [60]fullerene with the same carboxylic acids selectively gave another type of fullerene products, i.e., fullerenyl esters. Possible mechanisms for the formation of fullerene products are proposed.

Introduction

Various reactions of fullerenes have been developed to prepare a plethora of fullerene derivatives over the years.[1] Reactions of fullerenes promoted by metal salts are quite limited so far in comparison with the myriad reactions discovered in fullerene chemistry. Radical reactions were among the first to be investigated[2] and continue to be important methodologies for fullerene functionalizations.[1k,3] Recently, we have systematically investigated the radical reactions of [60]fullerene (C_{60}) mediated by manganese(III) acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$).[4,5] Meanwhile, two groups have illustrated the usage of lead(IV) acetate ($Pb(OAc)_4$) in fullerene chemistry.[6] Rubin and

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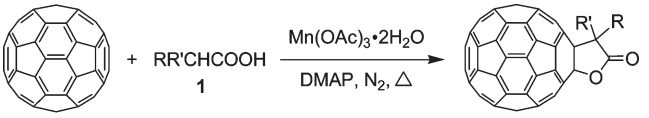
co-workers described the preparation of a novel compound with complete saturation of a single six-membered ring on C_{60} via a remarkable double 5-exo-trig addition reaction of alkoxyl radicals promoted by $Pb(OAc)_4$.[6a] Troshina et al. reported the formation of pyrrolidinofullerene derivatives by the $Pb(OAc)_4$-mediated oxidative coupling reaction of C_{60} with amino acid esters.[6b]

Only a few examples of fullerenyl esters have been known until now.[5d,7] The synthesis of fullerenyl esters was achieved either by conversion of ArC_{60}-H to ArC_{60}-OAc mediated by $Mn(OAc)_3 \cdot 2H_2O$[5d] or by esterification of fullerenols[7] and thus required multistep reactions starting from C_{60}. The number of synthesized C_{60}-fused lactones is also very limited. Four C_{60}-fused δ-lactones were prepared by us through the reaction of C_{60} with anthranilic acids and isoamyl nitrite in the presence of triethylamine.[8] Two C_{60}-fused γ-lactones were made by Foote's group via three steps beginning with C_{60}.[9] We reported the facile one-step synthesis of three C_{60}-fused γ-lactones by employing the $Mn(OAc)_3 \cdot 2H_2O$-mediated radical reaction of C_{60} with carboxylic acids, carboxylic anhydrides, or malonic acids.[5e] The obtained C_{60}-fused γ-lactones could be further transformed to fullerene hemiacetals, fullerene hemiketals, C_{60}-fused dihydrofurans, and fullerenols.[10] Obviously, more fullerenyl lactones and fullerenyl esters are in great demand for application and further functionalization. Herein, we extend our previous one-step protocol[5e] and give a full account for the synthesis of C_{60}-fused γ-lactones by the $Mn(OAc)_3 \cdot 2H_2O$-mediated reaction of C_{60} with various carboxylic acids. Interestingly, we also disclose that fullerenyl esters can be selectively obtained by the reaction of C_{60} with the same carboxylic acids in the presence of $Pb(OAc)_4$.

Results and Discussion

Although carboxylic acids, carboxylic anhydrides, and malonic acids could be employed to synthesize C_{60}-fused γ-lactones,[5e] carboxylic anhydrides and malonic acids as starting materials are relatively expensive and more difficult to attain than the corresponding carboxylic acids. Therefore, we decided to choose carboxylic acids as the reactants to extend the synthesis of C_{60}-fused γ-lactones. We had previously used acetic acid (**1a**), propionic acid (**1b**), and phenylacetic acid (**1c**).[5e] In the current work, additional six representative analogues, that is, *n*-butyric acid (**1d**), 3-phenylpropionic acid (**1e**), *n*-capronic acid (**1f**), *n*-caprylic acid (**1g**), lauric acid (**1h**), and stearic acid (**1i**), as well as carboxylic acids with two substituents at the α-position or with a functional group at the α-position, i.e., isobutyric acid (**1j**) and chloroacetic acid (**1k**), have been selected for the lactonization of C_{60}. Bases including 4-(dimethylamino)pyridine (DMAP), 1,8-diazabicyclo[5,4,0]undec-7-ene, pyridine, triethylamine, and triethylenediamine had been screened, and it was found that DMAP was superior to other bases.[5e] Metal salts such as $Mn(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$, and $(NH_4)_2Ce(NO_3)_6$ were also examined, and $Mn(OAc)_3 \cdot 2H_2O$ proved to be the best oxidant. Thus, the reaction of C_{60} with carboxylic acids **1d**−**k** giving C_{60}-fused γ-lactones **2d**−**k** was conducted by employing our previously established protocol[5e] (Scheme 1).

SCHEME 1. Reaction of C_{60} with Carboxylic Acids 1d−k and $Mn(OAc)_3 \cdot 2H_2O$ in the Presence of DMAP



1d, **2d**: R = C_2H_5, R' = H; **1e**, **2e**: R = CH_2Ph, R' = H;
1f, **2f**: R = $(CH_2)_3CH_3$, R' = H; **1g**, **2g**: R = $(CH_2)_5CH_3$, R' = H;
1h, **2h**: R = $(CH_2)_9CH_3$, R' = H; **1i**, **2i**: R = $(CH_2)_{15}CH_3$; R' = H;
1j, **2j**: R = R' = CH_3; **1k**, **2k**: R = Cl, R' = H

TABLE 1. Reaction Conditions and Product Yields Together with Recovered C_{60} for the $Mn(OAc)_3 \cdot 2H_2O$-Mediated Reaction of C_{60} with Carboxylic Acids 1a−k in the Presence of DMAP[a]

entry	substrate	R, R′	reaction time (min)	yield of **2**[b] (%)	recovered C_{60} (%)
1[c]	**1a**	H, H	60	24 (92)	74
2[c]	**1b**	CH_3, H	60	27 (93)	71
3	**1c**	Ph, H	30	34 (92)	63
4	**1d**	C_2H_5, H	60	9 (82)	89
5[d]	**1d**	C_2H_5, H	60	23 (70)	67
6	**1e**	$PhCH_2$, H	20	23 (92)	75
7	**1f**	C_4H_9, H	120	14 (64)	78
8[e]	**1f**	C_4H_9, H	30	20 (72)	72
9	**1g**	C_6H_{13}, H	120	9 (82)	89
10[e]	**1g**	C_6H_{13}, H	30	17 (61)	72
11	**1h**	$C_{10}H_{21}$, H	60	25 (81)	69
12	**1i**	$C_{16}H_{33}$, H	60	27 (84)	68
13[f]	**1j**	CH_3, CH_3	120	10 (34)	71
14	**1k**	Cl, H	15	23 (58)	60

[a]Unless otherwise specified, the molar ratio of C_{60}/**1**/$Mn(OAc)_3 \cdot 2H_2O$/DMAP = 1:20:2:1 and the reaction temperature = 140 °C. [b]Isolated yield. The yield in parentheses was based on consumed C_{60}. [c]Molar ratio of C_{60}/**1a** or **1b**/$Mn(OAc)_3 \cdot 2H_2O$/DMAP = 1:100:2:1. [d]Molar ratio of C_{60}/**1d**/$Mn(OAc)_3 \cdot 2H_2O$/DMAP = 1:50:2:1. [e]The reaction was performed at 180 °C. [f]17% of product **3j** was also obtained.

The reaction under the given experimental conditions was monitored by thin-layer chromatography (TLC) and/or high-performance liquid chromatography (HPLC) and stopped at the desired time to get the best product yield. The reaction conditions and product yields together with recovered C_{60} for the $Mn(OAc)_3 \cdot 2H_2O$-mediated reaction of C_{60} with carboxylic acids **1d**−**k** in the presence of DMAP along with those of carboxylic acids **1a**−**c**[5e] are listed in Table 1.

As seen from Table 1, all of the examined carboxylic acids **1a**−**k** afforded the desired lactones in 9−34% isolated yields (34−93% yields based on consumed C_{60}). The isolated yield of lactone **2k** should be lower than the actual value because of its decomposition and/or absorption on the silica gel during column chromatography. Phenylacetic acid (**1c**) under the same reaction conditions afforded higher isolated yield than other carboxylic acids (**1a**,**b**,**d**−**k**) presumably because the phenyl group could stabilize the formed α-*C*H

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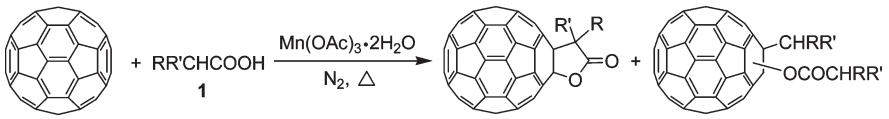
SCHEME 2. Reaction of C_{60} with Carboxylic Acids 1a−k Promoted by $Mn(OAc)_3 \cdot 2H_2O$ in the Absence of a Base



1a, **2a**, **3a**: R = R' = H; **1b**, **2b**, **3b**: R = CH_3, R' = H; **1c**, **2c**, **3c**: R = Ph, R' = H;
1d, **2d**, **3d**: R = C_2H_5, R' = H; **1e**, **2e**, **3e**: R = CH_2Ph, R' = H; **1f**, **2f**, **3f**: R = $(CH_2)_3CH_3$, R' = H;
1g, **2g**, **3g**: R = $(CH_2)_5CH_3$, R' = H; **1h**, **2h**, **3h**: R = $(CH_2)_9CH_3$, R' = H; **1i**, **2i**, **3i**: R = $(CH_2)_{15}CH_3$, R' = H;
1j, **2j**, **3j**: R = R' = CH_3; **1k**, **2k**, **3k**: R = Cl, R' = H

radical. The isolated yields of C_{60}-fused lactones could be significantly improved by increasing the amount of carboxylic acid (**1d**) from 20 to 50 equiv (entry 4 vs entry 5) or raising the reaction temperature (**1f**,**g**) from 140 to 180 °C (entries 7 and 9 vs entries 8 and 10). It should be noted that for the reaction of C_{60} with **1j** at 140 °C 17% yield of product **3j** (vide infra) was also formed in addition to 10% yield of lactone **2j** (entry 13). The formation of product **3j** could not be avoided completely by decreasing the temperature even to 100 °C. For the reaction of C_{60} with **1j** at 100 °C for 11 h, the yield of product **3j** decreased to 3%, while that of lactone **2j** dropped to 8% despite the much longer reaction time due to the lower reactivity of the reagents at lower temperature. Unfortunately, cyanoacetic acid, acetoacetic acid, succinic acid, and adipic acid could not react with C_{60} in *o*-dichlorobenzene to afford the corresponding lactones. It was reported that the very electron-deficient cyanoacetate radical added poorly to the already electron-deficient unsaturated ester (9% yield), whereas the complexed acetate radical added in 57% yield.[11] The C_{60} skeleton is more electron-deficient than an unsaturated ester. Therefore, it was not surprising that cyanoacetic acid and acetoacetic acid failed to react with C_{60}. In addition, both cyanoacetic acid and acetoacetic acid tended to decompose, especially at a higher temperature used for the lactonization of C_{60}. Succinic acid and adipic acid did not react with C_{60} probably due to their poor solubility in *o*-dichlorobenzene.

Just like lactones **2a**−**c**,[5e] the structures of lactones **2d**−**k** were fully established by their MS, ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectra. All lactones **2d**−**k** exhibited correct molecular weights in their high-resolution mass spectra. Their ^{1}H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. In their ^{13}C NMR spectra, besides the peaks for the addends including the signals at 168.37−179.23 ppm for the lactone moiety, there were at least 46 peaks containing some overlapped ones in the range of 133−155 ppm for the 58 sp^2-carbons of the C_{60} skeleton and two peaks at 95.91−96.59 ppm and 65.89−67.20 ppm for the two sp^3-carbons of the C_{60} moiety for lactones **2d**−**i** and **2k**, consistent with the C_1 symmetry of their molecular structures, whereas there existed only 28 lines including two overlapping ones in the range of 135−152 ppm for the 58 sp^2-carbons of the C_{60} cage and two peaks at 95.61 and 71.00 ppm for the two sp^3-carbons of the C_{60} skeleton for lactone **2j**, agreeing well with its C_s symmetry. The chemical shifts at 95.61−96.59 ppm and 65.89−71.00 ppm for the two sp^3-carbons of the C_{60} skeleton are close to the reported data of other C_{60}-fused lactones.[5e,8,9] In their IR spectra, the absorption at 1780−1791 cm^{-1} also demonstrated the presence of the lactone moiety, and the peaks at ca. 1430, 1185, 575, and 525 cm^{-1} corresponded to the fullerene skeleton. Their UV−vis spectra exhibited absorptions at ca. 255, 316, 416, and 687 nm, near to that in the previously reported C_{60}-fused lactones.[5e,8,9]

We found that the presence of DMAP proved to be crucial for the exclusive formation of lactones **2a**−**k** from the reaction of C_{60} with carboxylic acids **1a**−**k**. Other products were generated without the addition of DMAP. In order to ascertain the exact structures of these products, we explored the $Mn(OAc)_3 \cdot 2H_2O$-mediated radical reaction of C_{60} with carboxylic acids **1a**−**k** in the absence of DMAP. To our delight, we obtained the scarce fullerenyl esters **3a**−**j** besides lactones **2a**−**k** (Scheme 2).

The reaction conditions and product yields along with recovered C_{60} for the $Mn(OAc)_3 \cdot 2H_2O$-mediated reaction of C_{60} with carboxylic acids **1a**−**k** in the absence of a base are summarized in Table 2.

As can be seen from Table 2, both fullerenyl lactones and fullerenyl esters were generally formed for most carboxylic acids (**1b**,**d**−**i**) except for acetic acid (**1a**), phenylacetic acid (**1c**), isobutyric acid (**1j**), and chloroacetic acid (**1k**). In the case of acetic acid, only a trace amount of fullerenyl ester **3a** was obtained with the predominant formation of C_{60}-fused lactone **2a**. Phenylacetic acid was very reactive and afforded 1,4-$C_{60}(CH_2Ph)_2$[12] in 13% yield along with some unknown products instead of the desired C_{60}-fused lactone **2c** and fullerenyl ester **3c** at 140 °C for 30 min. The formation of 1,4-$C_{60}(CH_2Ph)_2$ should be ascribed to the addition to C_{60} by the benzyl radical, which was produced in situ from phenylacetic acid under our experimental conditions (vide infra). We therefore investigated this reaction at lower temperature (70 °C) and successfully obtained fullerenyl ester **3c** besides some unknown products and a trace amount of fullerenyl lactone **2c**. Control experiments showed that fullerenyl ester **3c** was stable at 100 °C, yet decomposed rapidly at 140 °C, whereas lactone **2c** remained unchanged at 140 °C for a long time. Therefore, the low yields of lactone **2c** and fullerenyl ester **3c** at the reaction temperature of 70 °C did not arise from the thermal instability of the products, but was attributed to the side reactions resulting in the unknown products owing to the high reactivity of **1c**. For the unknown products at 140 °C the decomposition of **3c** (if formed at 140 °C) might partially contribute to their formation. Similar to phenylacetic acid, isobutyric acid gave exclusively fullerenyl ester **3j** with negligible amount of lactone **2j**. In contrast, the

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TABLE 2. Reaction Conditions and Product Yields along with Recovered C_{60} for the $Mn(OAc)_3 \cdot 2H_2O$-Mediated Reaction of C_{60} with Carboxylic Acids 1a−k[a]

entry	substrate	R, R′	reaction time (h)	yield of **2**[b] (%)	yield of **3**[b,c] (%)	isomer ratio[d]	recovered C_{60} (%)
1[e]	**1a**	H, H	2	11 (61)	trace		82
2[e]	**1b**	CH_3, H	1	29 (74)	7 (18)	86/14	61
3[f]	**1c**	Ph, H	3	trace	11 (33)	67/33	67
4	**1d**	C_2H_5, H	3	7 (29)	14 (58)	88/12	76
5	**1e**	$PhCH_2$, H	2	17 (53)	9 (28)	76/24	68
6	**1f**	C_4H_9, H	2	16 (55)	8 (28)	88/12	71
7	**1g**	C_6H_{13}, H	3	9 (47)	8 (42)	93/7	81
8	**1h**	$C_{10}H_{21}$, H	3	16 (47)	16 (47)	95/5	66
9	**1i**	$C_{16}H_{33}$, H	3	16 (48)	15 (45)	93/7	67
10	**1j**	CH_3, CH_3	0.5	trace	31 (70)	100/0	56
11	**1k**	Cl, H	0.25	12 (34)	[g]	[g]	65

[a]Unless otherwise specified, the molar ratio of C_{60}/**1**/$Mn(OAc)_3 \cdot 2H_2O$ = 1:20:2 and the reaction temperature = 140 °C. [b]Isolated yield. The yield in parentheses was based on consumed C_{60}. [c]Total yield of 1,2-isomer and 1,4-isomer. [d]Refers to the ratio of 1,4-isomer/1,2-isomer. The 1,4-isomer/1,2-isomer ratio was determined by ^{1}H NMR spectroscopy. [e]Molar ratio of C_{60}/**1a** or **1b**/$Mn(OAc)_3 \cdot 2H_2O$ = 1:100:2. [f]The reaction was performed at 70 °C. [g]The formation of **3k** could not be ascertained, and thus, the isomeric ratio was not available.

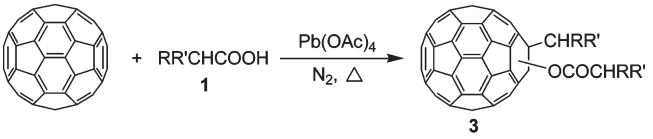
$Mn(OAc)_3 \cdot 2H_2O$-mediated reaction of C_{60} with chloroacetic acid in the absence of DMAP at 140 °C gave lactone 2k in 12% isolated yield and another product, which was not the expected fullerenyl ester **3k** based on the obtained spectral data, and its structure remains unassigned now. The formation of fullerenyl ester **3k** could not be ascertained as further separation of the rest minor products was very difficult. However, we could conclude that even if fullerenyl ester **3k** was produced it was only a very minor product. For all fullerenyl esters (**3a**−**i**) except **3j**, both 1,2-isomer and 1,4-isomer were observed. The predominant isomer of fullerenyl esters (**3b**−**i**) was determined as the 1,4-isomer. In most cases, the attempt to separate out the minor isomer from the major isomer through column chromatography was unsuccessful except for a few fullerenyl esters, that is, **3a**, **3b**, and **3e**. Interestingly, fullerenyl ester 3j existed only as the 1,4-isomer because the strong steric hindrance between the bulky $(CH_3)_2CH$ group and $(CH_3)_2CHCOO$ group, hence preventing the formation of the 1,2-isomer.

The poor selectivity for the formation of fullerenyl esters relative to C_{60}-fused lactones shown in Table 2 prompted us to explore other reaction conditions to selectively obtain fullerenyl esters (**3a**−**j**). Fortunately, this goal was achieved by conducting the reaction of C_{60} with carboxylic acids **1a**−**j** promoted by $Pb(OAc)_4$ instead of $Mn(OAc)_3 \cdot 2H_2O$ (Scheme 3).

The reaction conditions and product yields along with recovered C_{60} for the $Pb(OAc)_4$-promoted reaction of C_{60} with carboxylic acids **1a**−**j** are listed in Table 3.

The reaction of C_{60} with carboxylic acids **1a**−**j** promoted by $Pb(OAc)_4$ selectively gave fullerenyl esters **3a**−**j**. Phenylacetic acid (**1c**) gave 1,4-$C_{60}(CH_2Ph)_2$ in 11% yield along with some unknown products rather than the corresponding fullerenyl ester (**3c**) at 140 °C for 30 min, which were analogous to those obtained for the reaction of C_{60} with phenylacetic acid (**1c**) promoted by $Mn(OAc)_3 \cdot 2H_2O$ in the absence of DMAP at 140 °C. Similarly, we also investigated this reaction at lower temperature (100 °C) and exclusively obtained the fullerenyl ester (**3c**). For all fullerenyl esters **3a**−**i**, both 1,4-isomer and 1,2-isomer were also observed. As seen from the data listed in Tables 2 and 3, no obvious variations were found for the ratios of 1,4-isomer/1,2-isomer with the change of metal salts from $Mn(OAc)_3 \cdot 2H_2O$ to $Pb(OAc)_4$. The reaction temperature also had little effect

SCHEME 3. Reaction of C_{60} with Carboxylic Acids 1a−j Promoted by $Pb(OAc)_4$



1a, **3a**: R = R' = H; **1b**, **3b**: R = CH_3, R' = H;
1c, **3c**: R = Ph, R' = H; **1d**, **3d**: R = C_2H_5, R' = H;
1e, **3e**: R = CH_2Ph, R' = H; **1f**, **3f**: R = $(CH_2)_3CH_3$, R' = H;
1g, **3g**: R = $(CH_2)_5CH_3$, R' = H; **1h**, **3h**: R = $(CH_2)_9CH_3$, R' = H;
1i, **3i**: R = $(CH_2)_{15}CH_3$, R' = H; **1j**, **3j**: R = R' = CH_3

TABLE 3. Reaction Conditions and Product Yields along with Recovered C_{60} for the $Pb(OAc)_4$-Mediated Reaction of C_{60} with Carboxylic Acids 1a−j[a]

entry	substrate	R, R′	reaction time (h)	yield of **3**[b,c] (%)	isomer ratio[d]	recovered C_{60} (%)
1[e]	**1a**	H, H	1.5	16 (80)	17/83	80
2[e]	**1b**	CH_3, H	2.5	27 (75)	81/19	64
3[f]	**1c**	Ph, H	3	11 (58)	68/32	81
4	**1d**	C_2H_5, H	3	18 (67)	89/11	73
5	**1e**	$PhCH_2$, H	3	25 (71)	80/20	65
6	**1f**	C_4H_9, H	2.5	22 (44)	91/9	50
7	**1g**	C_6H_{13}, H	3	20 (71)	94/6	72
8	**1h**	$C_{10}H_{21}$, H	3	15 (68)	98/2	78
9	**1i**	$C_{16}H_{33}$, H	3	14 (58)	95/5	76
10	**1j**	CH_3, CH_3	0.5	25 (78)	100/0	68

[a]Unless otherwise specified, the molar ratio of C_{60}/**1**/$Pb(OAc)_4$ = 1:20:2 and the reaction temperature = 140 °C. [b]Isolated yield. The yield in parentheses was based on consumed C_{60}. [c]Total yield of 1,2-isomer and 1,4-isomer. [d]Refers to the ratio of 1,4-isomer/1,2-isomer. The 1,4-isomer/1,2-isomer ratio was determined by ^{1}H NMR spectroscopy. [e]Molar ratio of C_{60}/**1a** or **1b**/$Pb(OAc)_4$ = 1:100:2. [f]The reaction was performed at 100 °C.

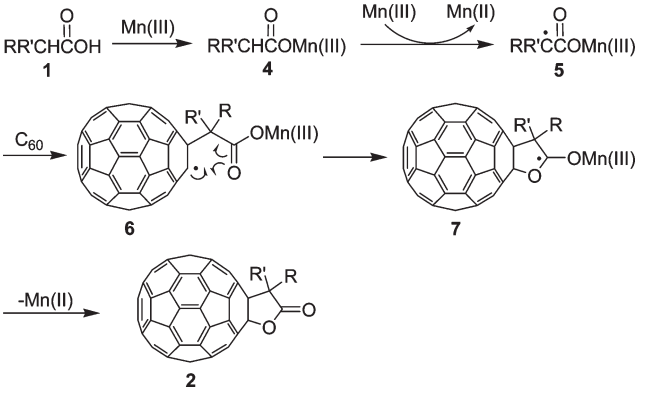
on the ratios of 1,4-isomer/1,2-isomer. For example, the $Pb(OAc)_4$ reaction of C_{60} with 3-phenylpropionic acid at 180 °C for 20 min afforded the 1,4-isomer and 1,2-isomer of **3e** in a ratio of 73:27, slightly different from the ratio of 80:20 for the same reaction at 140 °C for 3 h. For fullerenyl ester **3a**, the 1,2-adduct was the predominant isomer. The opposite selectivity for **3a** compared with **3b**−**j** was due to the less

steric hindrance between the methyl and acetoxy groups in the 1,2-isomer of **3a**. In comparison, only the 1,4-isomer of fullerenyl ester **3j** could be identified from the $Pb(OAc)_4$-mediated reaction of **1j** with C_{60}, just as the $Mn(OAc)_3 \cdot 2H_2O$-mediated reaction in the absence of DMAP. The reaction of C_{60} with chloroacetic acid mediated by $Pb(OAc)_4$ also afforded the same unidentified product as that observed in the reaction mediated by $Mn(OAc)_3 \cdot 2H_2O$ in the absence of DMAP. No evidence could be obtained for the formation of fullerenyl ester **3k**.

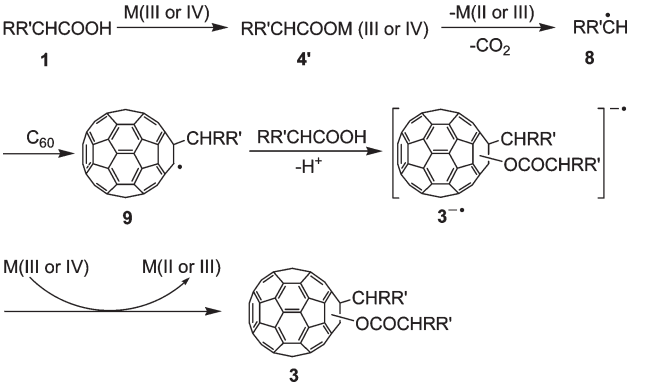
The identities of the major isomers of fullerenyl esters **3a**−**j** were fully established by HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. Their MALDI FT-ICR mass spectra with 2,5-dihydroxybenzoic acid as the matrix showed the $[M - RR'CHCOO]^+$ peak due to easy loss of the carboxylate group under the mass experimental conditions. However, the existence of the ester group in **3a**−**j** was supported by the absorption at 1742−1751 cm^{-1} in their IR spectra. The assigned structures were further confirmed by their NMR and UV−vis spectral data. Because 1,2-isomers and/or 1,4-isomers were obtained for fullerenyl esters **3a**−**j**, it is worthwhile to compare their ^{1}H NMR, ^{13}C NMR, and UV−vis spectra. In the ^{1}H NMR spectra of fullerenyl esters **3a**−**i**, the chemical shifts for the protons on the carbon atom adjacent to the carboxyl group together with protons on the carbon atom attached to the C_{60} core in the 1,2-isomers were obviously shifted downfield relative to those in the 1,4-isomers. In their ^{13}C NMR spectra, the 1,2- and 1,4-isomers of fullerenyl esters **3a**−**j** showed different spectral patterns. The 1,4-isomers of **3b**−**j** exhibited at least 50 peaks including some overlapped ones due to the 58 sp^2-carbons of the fullerene moiety, consistent with the C_1 symmetry of their molecular structures. The sp^3-carbons of the C_{60} cage appeared at 58.11−63.40 ppm and 76.74−79.00 ppm. However, the 1,2-isomer of **3a** exhibited only 29 lines for the sp^2-carbons of the C_{60} skeleton including one overlapped peak, which agrees well with its C_s molecular symmetry. The two sp^3-carbons of the C_{60} cage were located at 61.54 and 92.95 ppm. The δ_c at 92.95 ppm for the 1,2-isomer of **3a** corresponds to the fullerenyl sp^3-carbon connecting to the oxygen atom of the carbonyl group, and the chemical shift is shifted downfield more than 13.95 ppm relative to those (76.74−79.00 ppm) in the 1,4-isomers of **3b**−**i** as well as in other similar 1,4-adducts.[5d,7d] The UV−vis spectrum for the 1,2-isomer of **3a** showed a peak at 417 nm, which is a characteristic peak for a 1,2-adduct with an oxygen atom directly attached to the fullerene cage.[5e,8,9] In comparison, the UV−vis spectra for the 1,4-isomer of **3b**−**j** displayed a typical absorption at 441−446 nm for a 1,4-adduct.[7d] However, the ^{13}C NMR chemical shift (170.86−174.13 ppm) and infrared absorption (1742−1751 cm^{-1}) for the ester carbonyl group of **3a**−**j** were close to each other.

The $Mn(OAc)_3 \cdot 2H_2O$-mediated reaction of C_{60} and carboxylic acids **1** generally afforded lactones **2** in the presence or absence of DMAP. However, the presence of DMAP seemed to suppress the formation of fullerenyl esters **3**. To account for the production of lactones **2** in the presence and absence of DMAP, we propose a reaction mechanism (Scheme 4), which is slightly different from our previous one.[5e]

SCHEME 4. Mechanism for the Formation of C_{60}-Fused Lactones 2a−k from C_{60} and Carboxylic Acids 1a−k



SCHEME 5. Proposed Mechanism for the Formation of Fullerenyl Esters 3a−j from C_{60} and Carboxylic Acids 1a−j



Carboxylic acid **1** reacts with $Mn(OAc)_3$ to afford manganese(III) carboxylate **4**,[5e,11a,13] which is oxidized by another molecule of $Mn(OAc)_3$ to generate radical **5**.[5e,11a] Addition of radical **5** to C_{60} gives fullerenyl radical **6**, which cyclizes to radical **7**. Finally, loss of Mn(II) species from **7** provides lactone **2**.[5e,11a] Bases such as potassium acetate is known to accelerate the reaction rate and yield of lactonization reactions by effecting the deprotonation of carboxylates **4**.[11a] DMAP may also act as an enhancer for the fullerene-fused lactones **2** besides as a suppressor for the fullerenyl esters **3**.

The possible formation mechanism for fullerenyl esters **3a**−**j** arising from the reaction of C_{60} with carboxylic acids promoted by $Pb(OAc)_4$ or $Mn(OAc)_3 \cdot 2H_2O$ is shown in Scheme 5.

The carboxylic acid **1** reacts with $Pb(OAc)_4$ or $Mn(OAc)_3 \cdot 2H_2O$ to give lead(IV) carboxylate or manganese(III) carboxylate **4′**, and subsequent decarboxylation generates alkyl radical **8**.[13] The addition of alkyl radical **8** to C_{60} produces fullerenyl radical **9**. Oxygen nucleophiles such as alkoxides[14] and phenols[1n] are known to add to the C_{60} cage. Furthermore, the addition of nucleophiles to fullerenyl radicals has been proposed in the literature.[7d,14b,15] Therefore, it is

(13) Serguchev, Yu. A.; Beletskaya, I. P. *Russ. Chem. Rev.* **1980**, *49*, 1119.

(14) (a) Wang, G.-W.; Shu, L.-H.; Wu, S.-H.; Wu, H.-M.; Lao, X.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1071. (b) Wang, G.-W.; Lu, Y.-M.; Chen, Z.-X.; Wu, S.-H. *J. Org. Chem.* **2009**, *74*, 4841.

(15) Wang, G.-W.; Li, F.-B.; Chen, Z.-X.; Wu, P.; Cheng, B.; Xu, Y. *J. Org. Chem.* **2007**, *72*, 4779.

reasonable to assume that carboxylic acid **1** can add to fullerenyl radical **9** with the loss of H^+ to give radical anion $\mathbf{3}^{-\bullet}$. Oxidation of radical anion $\mathbf{3}^{-\bullet}$ by Mn(III) or Pb(IV) species affords fullerenyl ester **3**.

Experimentally, the reaction of C_{60} with carboxylic acids promoted by $Mn(OAc)_3 \cdot 2H_2O$ or $Pb(OAc)_4$ gave only unsymmetrical fullerene derivative **3**, which has an alkyl group and a carboxylic ester group. No symmetrical fullerene products bearing either two carboxylic ester groups ($C_{60}(OOCCHRR')_2$) or two alkyl groups ($C_{60}(CHRR')_2$) except for $C_{60}(CH_2Ph)_2$ could be isolated. Products $C_{60}(OOCCHRR')_2$ were not obtained probably due to the inaccesibility of acyloxy radical RR′CHCOO, which would be too unstable and readily loss CO_2 to give alkyl radical **8**.[16] On the other hand, fullerenyl radical **9** prefers to react with large excess of RR′CHCOOH rather than couples with another molecule of radical **8** because the probability is extremely low for radical **9** to capture radical **8** due to the very low concentration of radical **8** relative to the starting reagent RR′CHCOOH. Among the carboxylic acids **1a**−**k**, phenylacetic acid lost CO_2 most readily and accumulated the highest concentration of benzyl radical, leading to the formation of $C_{60}(CH_2Ph)_2$ at 140 °C. Isobutyric acid also easily lost CO_2 to produce an isopropyl radical, a stable secondary radical. The fact that phenylacetic acid and isobutyric acid tend to lose CO_2 to give the benzyl and isopropyl radicals can explain why their reactions with C_{60} mediated by $Mn(OAc)_3 \cdot 2H_2O$ in the absence of DMAP did not afford the corresponding lactones, and the reaction of C_{60} with isobutyric acid mediated by $Mn(OAc)_3 \cdot 2H_2O$ in the presence of DMAP also generated fullerenyl ester **3j** besides fullerene-fused lactone **2j**. The failure to observe fullerenyl ester **3c** in the $Mn(OAc)_3 \cdot 2H_2O$-mediated reaction of C_{60} with phenylacetic acid in the presence of DMAP probably due to its facile decomposition at 140 °C.

Conclusion

The $Mn(OAc)_3 \cdot 2H_2O$-mediated radical reaction of C_{60} with carboxylic acids in the presence of DMAP exclusively led to the formation of C_{60}-fused lactones, while the same reaction without the addition of DMAP resulted in the generation of both C_{60}-fused lactones and fullerenyl esters. Interestingly, the fullerenyl esters could be selectively obtained when the reaction of C_{60} with carboxylic acids was promoted by $Pb(OAc)_4$ instead of $Mn(OAc)_3 \cdot 2H_2O$. Plausible reaction mechanisms are proposed to explain the formation of the fullerene products.

Experimental Section

General Procedure for the Synthesis of C_{60}-Fused Lactones 2d−k from the Reaction of C_{60} with Carboxylic Acids 1d−k and $Mn(OAc)_3 \cdot 2H_2O$ in the Presence of DMAP. A 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer was charged with C_{60} (43.2 mg, 0.06 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (32.2 mg, 0.12 mmol), and 4-(dimethylamino)pyridine (DMAP) (7.4 mg, 0.06 mmol). After the added compounds were completely dissolved in *o*-dichlorobenzene (10 mL) by sonication, 20 equiv of carboxylic acid **1** (also 50 equiv for **1d**) was added. The resulting solution was deoxygenated with nitrogen for 20 min, and then the mixture was heated with stirring in an oil bath preset at 140 °C (also 180 °C for **1f** and **1g**) under nitrogen atmosphere for a designated time (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 as the eluent to give unreacted C_{60} and then with carbon disulfide/toluene as the eluent to give lactone **2**.

2d: ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 4.41 (t, J = 7.0 Hz, 1H), 2.68−2.52 (m, 2H), 1.59 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$, all 1C unless indicated) δ 174.66, 154.58, 149.38, 147.98, 147.44, 146.35, 146.31 (2C), 146.26, 146.21, 146.19, 146.06, 146.05, 146.02, 145.92 (2C), 145.42, 145.40, 145.22, 145.10 (2C), 145.09 (2C), 145.07, 145.02, 144.84, 144.82, 144.40 (2C), 144.22, 144.15 (2C), 143.81, 142.74, 142.68, 142.54, 142.53, 142.47 (2C), 142.08, 142.04, 141.97, 141.94, 141.91, 141.89 (2C), 141.86, 141.47, 141.40, 141.16, 140.93, 139.97, 139.62, 139.58, 139.49, 137.40, 136.85, 136.81, 134.19, 95.91 (sp^3-*C* of C_{60}), 66.65 (sp^3-*C* of C_{60}), 50.65, 25.63, 12.74; FT-IR ν /cm^{-1} (KBr) 2924, 1780, 1509, 1460, 1432, 1268, 1219, 1187, 1166, 1015, 998, 957, 799, 769, 575, 562, 541, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.03), 316 (4.56), 416 (3.48), 686 (2.37); MALDI FT-ICR (2,5-dihydroxybenzoic acid as the matrix) MS *m*/*z* calcd for $C_{64}H_6O_2$ [M^+] 806.0368, found 806.0380.

2j: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 2.21 (s, 6H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$) (all 2C unless indicated) δ 179.23 (1C), 152.00, 148.36 (1C), 147.80 (1C), 146.61 (4C), 146.41, 146.39, 146.37, 146.20, 145.46, 145.42, 145.33, 145.20, 144.87 (4C), 144.63, 144.58, 143.04, 142.85, 142.77, 142.29, 142.26, 142.23, 142.06, 141.71, 141.38, 140.04, 139.96, 137.60, 135.83, 95.61 (1C, sp^3-*C* of C_{60}), 71.00 (1C, sp^3-*C* of C_{60}), 47.62 (1C), 28.06; FT-IR ν/cm^{-1} (KBr) 2922, 1781, 1459, 1430, 1385, 1256, 1185, 1145, 1098, 1011, 980, 961, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.10), 316 (4.62), 416 (3.61), 686 (2.52); MALDI FT-ICR MS (2,5-dihydroxybenzoic acid as the matrix) *m*/*z* calcd for $C_{64}H_6O_2$ [M^+] 806.0368, found 806.0376.

General Procedure for the Synthesis of C_{60}-Fused Lactones 2a−k and Fullerenyl Esters 3a−j from the $Mn(OAc)_3 \cdot 2H_2O$-Mediated Reaction of C_{60} with Carboxylic Acids 1a−k in the Absence of a Base. By following the same experimental procedure as for the preparation of C_{60}-fused lactones **2d**−**k** from the reaction of C_{60} with carboxylic acids **1d**−**k** promoted by $Mn(OAc)_3 \cdot 2H_2O$ in the presence of DMAP, the reaction of C_{60} (43.2 mg, 0.06 mol), $Mn(OAc)_3 \cdot 2H_2O$ (32.2 mg, 0.12 mmol), and a given amount of carboxylic acid **1** in the absence of DMAP gave unreacted C_{60}, fullerenyl ester **3**, and C_{60}-fused lactone **2**.

General Procedure for the Synthesis of Fullerenyl Esters 3a−j from the Reaction of C_{60} with Carboxylic Acids 1a−j Promoted by $Pb(OAc)_4$. C_{60} (43.2 mg, 0.06 mol), $Pb(OAc)_4$ (96%, 55.4 mg, 0.12 mol), and a given amount of carboxylic acid **1** were mixed in a 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. After the compounds were completely dissolved in *o*-dichlorobenzene (10 mL) by sonication, the resulting solution was deoxygenated with nitrogen for 20 min, and then the mixture was stirred and heated in an oil bath preset at 140 °C (100 °C for **1c**) under nitrogen atmospheric conditions until the reaction was complete (monitored by TLC). The reaction mixture 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 as the eluent to give unreacted C_{60} and then eluted with carbon disulfide/toluene to afford fullerenyl ester **3**.

3a: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$, promoted by $Pb(OAc)_4$) δ 3.18 (s, 2.48H, 1,2-isomer), 2.86 (s, 0.52H, 1,4-isomer), 2.60 (s, 2.48H, 1,2-isomer), 2.46 (s, 0.52H, 1,4-isomer); ^{1}H NMR (300 MHz, CS_2/$CDCl_3$, 1,2-isomer) δ 3.17 (s, 3H), 2.60 (s, 3H); ^{13}C

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NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated, 1,2-isomer) δ 171.50 (1C), 157.34, 148.71, 148.36 (1C), 147.59 (1C), 146.47, 146.26, 146.08, 146.01 (4C), 145.57, 145.23, 145.16, 145.06, 144.75, 144.55, 144.46, 144.36, 142.90, 142.54, 142.38, 142.26, 142.18, 142.09, 141.66, 141.17, 141.11, 140.03, 139.07, 138.12, 134.71, 92.95 (sp^3-*C* of C_{60}), 61.54 (sp^3-*C* of C_{60}), 27.62, 21.84; FT-IR ν/cm^{-1} (KBr) 2924, 2853, 1751, 1461, 1426, 1363, 1265, 1215, 1111, 1008, 980, 881, 769, 575, 555, 527; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (4.89), 315 (4.45), 417 (3.50), 687 (2.40); MALDI FT-ICR (2,5-dihydroxybenzoic acid as the matrix) MS *m*/*z* calcd for $C_{61}H_3$ $[M - CH_3COO]^+$ 735.0235, found 735.0228.

3b: ^1H NMR (300 MHz, $CS_2/CDCl_3$, promoted by $Mn(OAc)_3 \cdot 2H_2O$) δ 3.49 (q, $J = 7.5$ Hz, 0.28H, 1,2-isomer), 3.11 (q, $J = 7.5$ Hz, 1.72H, 1,4-isomer), 2.90 (q, $J = 7.5$ Hz, 0.28H, 1,2-isomer), 2.75 (q, $J = 7.5$ Hz, 1.72H, 1,4-isomer), 1.91 (t, $J = 7.5$ Hz, 0.42H, 1,2-isomer), 1.84 (t, $J = 7.5$ Hz, 2.58H, 1,4-isomer), 1.49 (t, $J = 7.5$ Hz, 0.42H, 1,2-isomer), 1.40 (t, $J = 7.5$ Hz, 2.58H, 1,4-isomer); ^1H NMR (300 MHz, $CS_2/CDCl_3$, promoted by $Pb(OAc)_4$) δ 3.50 (q, $J = 7.5$ Hz, 0.38H, 1,2-isomer), 3.10 (q, $J = 7.5$ Hz, 1.62H, 1,4-isomer), 2.88 (q, $J = 7.5$ Hz, 0.38H, 1,2-isomer), 2.73 (q, $J = 7.5$ Hz, 1.62H, 1,4-isomer), 1.90 (t, $J = 7.5$ Hz, 0.57H, 1,2-isomer), 1.83 (t, $J = 7.5$ Hz, 2.43H, 1,4-isomer), 1.48 (t, $J = 7.5$ Hz, 0.57H, 1,2-isomer), 1.39 (t, $J = 7.5$ Hz, 2.43H, 1,4-isomer); ^1H NMR (300 MHz, CS_2/DMSO-d_6, 1,4-isomer) δ 3.10 (q, $J = 7.5$ Hz, 2H), 2.70 (q, $J = 7.5$ Hz, 2H), 1.81 (t, $J = 7.5$ Hz, 3H), 1.36 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated, 1,4-isomer) δ 171.38, 154.45, 152.71, 151.86 147.67, 147.03, 146.32, 146.27, 146.22, 146.19, 145.92, 145.75, 145.70, 145.60, 145.50, 145.30, 145.19, 144.58, 144.48, 144.34 (2C), 144.22, 143.87, 143.70, 143.48, 143.35, 143.16, 143.00, 142.91, 142.89, 142.85 (2C), 142.77, 142.72 (2C), 142.65, 142.33, 142.24, 142.09, 141.93, 141.88, 141.70, 141.68, 141.59, 141.53, 141.48, 141.37, 141.25 (2C), 141.09, 140.96, 140.93, 140.43, 139.59, 139.37, 138.94, 138.59, 137.04, 136.16, 76.74 (sp^3-*C* of C_{60}), 58.59 (sp^3-*C* of C_{60}), 34.34, 27.27, 10.81, 8.56; FT-IR ν/cm^{-1} (KBr) 2961, 2925, 1748, 1510, 1455, 1428, 1379, 1351, 1266, 1152, 1075, 997, 978, 920, 881, 763, 583, 569, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (4.96), 323 (4.43), 444 (3.68), 687 (2.37); MALDI FT-ICR (2,5-dihydroxybenzoic acid as the matrix) MS *m*/*z* calcd for $C_{62}H_5$ $[M - CH_3CH_2COO]^+$ 749.0391, found 749.0410.

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Supporting Information Available: Spectral data of products **2e**−**i**,**k** and **3c**−**j**; NMR spectra of products **2d**−**k** and **3a**−**j**. This material is available free of charge via the Internet at http://pubs.acs.org.