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An Alternative Type of Fullerene Products from the Reaction of [60]Fullerene with Alkoxides and Subsequent Derivatization

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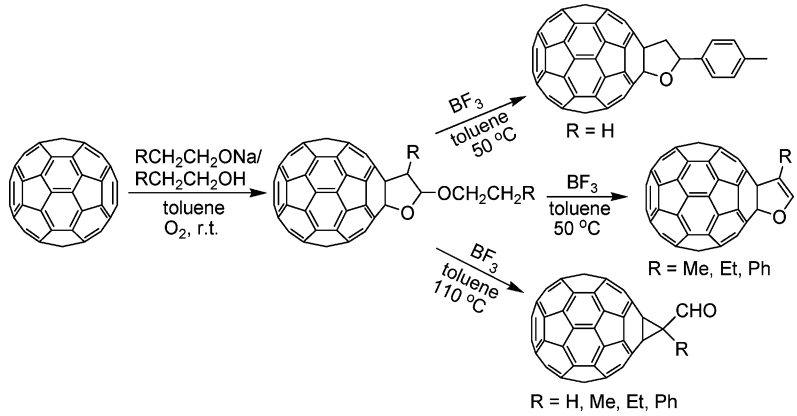

Reaction of [60]fullerene with freshly prepared RCH_2CH_2ONa/RCH_2CH_2OH (R = H, Me, Et, Ph) in anhydrous toluene in the presence of air unexpectedly afforded fullerene products with a C_{60}-fused tetrahydrofuran ring skeleton and an acetal moiety, which could be further transformed into C_{60}-fused dihydrofurans, tolyl-substituted C_{60}-fused tetrahydrofuran, and methanofullerenes bearing a formyl group by boron trifluoride etherate. Possible reaction mechanisms are proposed to explain the formation of different fullerene products.

Introduction

Various types of reactions to functionalize fullerenes have been described.[1] Among them nucleophilic addition is one of the first examined reactions. Grignard reagents, organolithium reagents, and amines have been widely employed to synthesize fullerene derivatives.[1] However, the reaction of [60]fullerene (C_{60}) with alkoxides has been scarcely investigated. Olah et al. were the first to treat fullerene derivatives $C_{60}Cl_n$ with MeOH/KOH or MeONa/MeOH and observed the formation of a mixture of polymethoxylated $C_{60}(OMe)_n$ (up to 26 methoxy groups determined by mass spectroscopy).[2] Similar result was obtained from the reaction of $C_{60}F_n$ with MeONa/MeOH.[3] Reaction of $C_{60}Cl_6$ with ArOH/KOH gave benzo[*b*]furano-[2,′3′:1,2][60]fullerene derivatives along with other products arising from substitution/elimination occurring across the 1,2-positions of the hexachloro precursor and nucleophilic replacement of some of the other chloro addends in the precursor by arenoxy groups.[4] Isolation of pure $C_{60}(OR)_5Cl$ was achieved by the reaction of $C_{60}Cl_6$ with RONa/ROH (R = Me, Et).[5]

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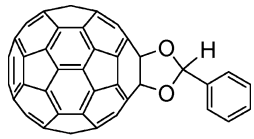
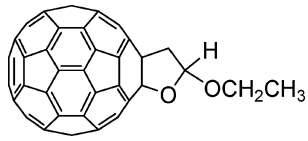


1

FIGURE 1. Structure of compound **1**.



2

FIGURE 2. Structure of compound **2**.

Nucleophilic addition of MeONa/MeOH to fullerene compounds bearing an epoxy group and/or *tert*-butylperoxy groups gave methoxylated derivatives.[6] On the other hand, Wilson and Wu reported that the addition of a MeONa/MeOH solution to C_{60} itself in toluene led to formation of $C_{60}(OMe)_n^-$ (n = 1, 3, 5, 7) as major anions as well as a product derived from coupling and oxidation with toluene, $C_{60}O_2(CH_2C_6H_5)^-$.[7] Nevertheless, attempts to isolate these products from the reaction mixture were not successful, and the adducts were only detected by ESI-MS. The anion $C_{60}(OMe)^-$ was also detected by mass and vis−near-IR spectroscopies from the reaction mixture of C_{60} and MeO^- in benzonitrile.[8] In 1995, we described the preparation of a C_{60}-fused 1,3-dioxolane derivative **1** (Figure 1) by the reaction of C_{60} with $PhCH_2ONa/PhCH_2OH$.[9] Even though we also conducted the reaction of C_{60} with EtONa/EtOH and isolated an adduct, we could not solve the structure of the product at that time. Herein we report the unexpected structure of the ethoxide-C_{60} adduct, and a systematic study on the novel reaction of C_{60} with other sodium alkoxides and subsequent functionalization of the obtained fullerene products.

Results and Discussion

The reaction of C_{60} with 10 equiv of EtONa/EtOH (freshly prepared by treating ethanol with sodium) in anhydrous toluene under aerobic conditions for 3 h afforded an ethoxide-C_{60} adduct, which was not a C_{60}-fused 1,3-dioxolane derivative with a structure similar to compound **1** but instead turned out to be a fullerene product containing a C_{60}-fused tetrahydrofuran ring skeleton and an acetal moiety, i.e., compound **2** (Figure 2).

The identity of compound **2** was fully established by its HRMS, ^{1}H NMR, ^{13}C NMR, HMQC, HMBC, UV−vis, and IR spectra. The HRMS (ESI) of product **2** gave a peak at 831.0416 for $C_{64}H_8NaO_2^+$, corresponding to the $[M + Na]^+$ ionic peak. In its ^{1}H NMR spectrum, the acetal proton appeared as a double doublet at 6.15 ppm, split by the adjacent methylene protons. The observed small coupling constants (J = 3.3, 1.2 Hz) have precedents in tetrahydrofuran derivatives containing a similar acetal moiety.[10,11] The two CH_2O protons were nonequivalent. One proton as a dq multiplet was located at 4.32 ppm (J = 9.5, 7.1 Hz), and another proton with the same splitting pattern was embedded in 3.88−3.99 ppm. In the ^{13}C NMR spectrum of compound **2**, there were 43 peaks with some overlapping ones in the range of 134−156 ppm for the 58 sp^2-carbons of the fullerene skeleton, consistent with its molecular structure with C_1 symmetry. The two sp^3-carbons of the C_{60} cage were located at 66.71 and 98.41 ppm, while the acetal carbon appeared at 102.68 ppm. The chemical shifts for the sp^3-carbons of the C_{60} skeleton connecting the oxygen atom and the acetal carbon in compound **2** were close to those in compound **1**[9] and other similar compounds.[11] The structure assignment of product **2** was further confirmed by its HMQC and HMBC spectra, which clearly demonstrated that the two nonequivalent protons (~3.9 and 4.32 ppm) were bound to the CH_2O carbon (63.00 ppm) and that the proton at 6.15 ppm was connected to the acetal carbon (102.68 ppm) and showed a three-bond correlation with the sp^3-carbon of the C_{60} skeleton at 98.41 ppm. The UV−vis spectrum of product **2** showed a peak at 427 nm, which is the characteristic peak for a 1,2-adduct of C_{60}.[11]

Further investigation revealed that alkoxide/alcohol mixtures prepared from primary alcohols bearing β-hydrogen could react with C_{60}, and afforded fullerene derivatives with a structure similar to compound **2** rather than compound **1**. The reaction of C_{60} with 10 equiv of ^{n}PrONa/^{n}PrOH, ^{n}BuONa/^{n}BuOH, and $PhCH_2CH_2ONa/PhCH_2CH_2OH$ in anhydrous toluene in the presence of air gave products **3**, **4**, and **5**, respectively (Scheme 1).

For products **3**−**5**, there existed two (*cis* and *trans*) isomers, depending on the orientations of the R and RCH_2CH_2O groups. These two isomers could be separated by flash column chromatography over silica gel with carbon disulfide as the eluent.

The reaction times, product yields, and *cis*/*trans* isomeric ratios along with recovered C_{60} for the reaction of C_{60} with 10 equiv of alkoxides at room temperature affording products **2**−**5** are listed in Table 1. It should be pointed out that the reaction of C_{60} with ethoxide gave lower product yield (14%) and less recovered C_{60} (9%) compared with the reaction of C_{60} with other alkoxide. When the reaction time for the mixture of C_{60} and ethoxide was shortened from 3 to 1.5 h, product **2** was obtained in slightly lower yield (9%) but with much higher recovery of C_{60} (62%). These results may hint that ethoxide is more reactive than other alkoxide. Some unidentified byproducts, which may contain multiadducts as detected by ESI-MS for the reaction of C_{60} with methoxide,[7] were observed in the reaction of C_{60} with alkoxides.

Products *cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, and *trans*-**5** were fully characterized by HRMS, ^{1}H NMR, ^{13}C NMR, UV−vis, and IR spectra. It is noteworthy that in the ^{1}H NMR spectra of the *cis* and *trans* isomers of products **3**−**5**, the coupling constants $^3J_{HH}$ between the adjacent methine protons were small (~4 Hz) for the *cis* isomers and diminished to zero for the *trans* isomers.[10,11] The assignments for the *cis* and *trans* isomers were further confirmed by the calculated coupling constants by modified Karplus equation. For example, the calculated coupling constants for the *cis* and *trans* isomers of **3** were 6.5 and 2.5

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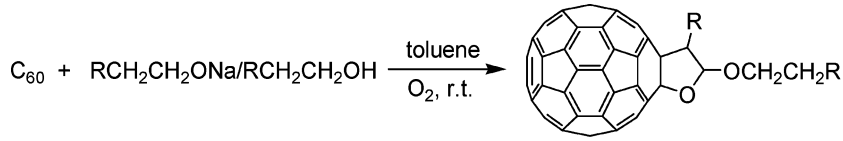
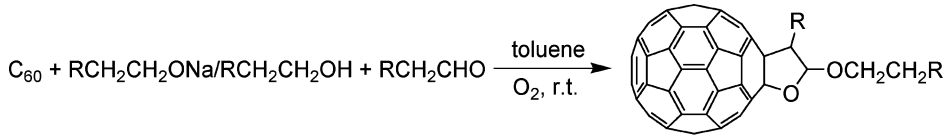
(12) The HLA (4 substituents) equation as modified Karplus equation implemented in the free available MestReJ program was employed to calculate coupling constants. The input dihedral angels of 19.5° and 114.6° for *cis*-**3** and *trans*-**3**, respectively, were obtained from the AM1-optimized structures.

SCHEME 1. Reaction of C_{60} with Alkoxides



2: R = H; **3**: R = CH_3; **4**: R = CH_2CH_3; **5**: R = Ph

SCHEME 2. Reaction of C_{60} with Alkoxides and Aldehydes



2: R = H; **3**: R = CH_3; **4**: R = CH_2CH_3; **5**: R = Ph

TABLE 1. Reaction Times, Yields, *cis*/*trans* Ratios, and Recovered C_{60} for the Reaction of C_{60} with Alkoxides

product	reaction time (h)	yield (%)[a]	*cis*/*trans* ratio	recovered C_{60} (%)
2	3	14		9
3	3	40	21/19	39
4	3	22	16/6	62
5	6	20	9/11	47

[a] Total yield for the *cis* and *trans* isomers of **3**, **4**, and **5**.

TABLE 2. Reaction Times, Yields, *cis*/*trans* Ratios, and Recovered C_{60} for the Reaction of C_{60} with Alkoxides and Aldehydes

product	reaction time (h)	yield (%)[a]	*cis*/*trans*	recovered C_{60} (%)
2[b]	0.5	22		63
3	2	43	25/18	52
4	2	28	20/8	47
5	6	25	12/13	38

[a] Total yield for the *cis* and *trans* isomers of **3**, **4**, and **5**. [b] Excess gaseous acetaldehyde was slowly bubbled into the reaction mixture of C_{60} and EtONa/EtOH.

Hz (Δ = 4.0 Hz),[12] which correlate well with their observed 3.9 and 0.0 Hz (Δ = 3.9 Hz), respectively. In the ^{13}C NMR spectra of products **3**−**5**, the two sp^3-carbons of C_{60} skeletons and the acetal carbon were located at 70.96−73.35, 98.09−99.41, and 104.04−109.78 ppm, respectively. These data were close to those in compound **2** and other similar compounds.[11] Furthermore, the ^{13}C NMR chemical shifts of the acetal carbons in the *cis* isomers (104.04−105.51 ppm) were shifted upfield about 4−5 ppm relative to those in the *trans* isomers (107.90−109.78 ppm). The same phenomenon has been observed previously by us.[11b]

We found that even though the alkoxide/alcohol mixtures prepared from 1-propanol and 2-phenylethanol reacted with C_{60}, those from the isomeric secondary alcohols, i.e., 2-propanol and 1-phenylethanol, failed to react with C_{60} to give the desired products. In addition, no corresponding fullerene product could be isolated from the reaction of C_{60} with the alkoxide/alcohol mixture made from a tertiary alcohol such as *tert*-butanol. These results implied that alkoxide/alcohol mixtures prepared only from primary alcohols bearing β-hydrogen could react with C_{60} to give fullerene products with a C_{60}-fused tetrahydrofuran ring skeleton and an acetal moiety.

We recently reported that the reaction of C_{60} with aldehydes/ketones and alkoxides gave fullerene products with a skeleton similar to that of products **2**−**5**.[11b] We surmised that the same reaction mechanism might be operated for the reaction of C_{60} with alkoxides affording products **2**−**5** if the corresponding aldehydes could be formed in situ from the RCH_2CH_2ONa/RCH_2CH_2OH mixtures under our experimental conditions. To our delight, we found that the reaction of C_{60} with RCH_2CH_2ONa/RCH_2CH_2OH (R = H, Me, Et, Ph) and the corresponding aldehyde RCH_2CHO (R = H, Me, Et, Ph) indeed gave products **2**−**5** (Scheme 2) with nearly the same *cis*/*trans* isomeric ratios, but the reaction was faster and the yield was higher compared with the reaction of C_{60} with RCH_2CH_2ONa/RCH_2CH_2OH alone. The reaction times, product yields, *cis*/*trans* isomeric ratios along with recovered C_{60} for the reaction of C_{60} with 10 equiv of alkoxides and 1 equiv of aldehydes at room temperature affording products **2**−**5** are listed in Table 2.

It is interesting to observe that reactions of $PhCH_2ONa$/$PhCH_2OH$ and $PhCH_2CH_2ONa$/$PhCH_2CH_2OH$ with C_{60} gave different types of products, i.e., adduct **1** and adduct **5**, respectively. It should be also emphasized that only one molecule of $PhCH_2O^-$ was incorporated into adduct **1**, whereas apparently two molecules of $RCH_2CH_2O^-$ were integrated into products **2**−**5**. Obviously, the reaction pathways to generate product **1** and products **2**−**5** were completely different. No reaction occurred when oxygen was excluded from the reaction mixture of C_{60} and RCH_2CH_2ONa/RCH_2CH_2OH (R = H, Me, Et, Ph). Therefore, oxygen played a crucial role in the success of the above reactions to give products **2**−**5**. Although how alkoxides RCH_2CH_2ONa were oxidized to aldehydes RCH_2CHO under our reaction conditions is difficult to know now, their formation might first involve the electron transfer between C_{60} and $RCH_2CH_2O^-$ to give $C_{60}^{-\bullet}$ and $RCH_2CH_2O^{\bullet}$.[7,8] The α-hydrogen of the alkoxy radical $RCH_2CH_2O^{\bullet}$ is abstracted by $C_{60}^{-\bullet}$ radical anion or other radical species including another alkoxyl radical to give aldehydes RCH_2CHO,[13] as shown in Scheme 3. The increase in reaction rates and product yields after purposive addition of aldehydes to the reaction mixtures of C_{60} and alkoxides suggested the involvement of aldehydes in the reactions. One possible mechanism, i.e., path (i) in Scheme 3, for the formation of products **2**−**5** from the reaction of C_{60} with alkoxides is the same as that for the reaction of C_{60} with aldehydes and alkoxides and had been presented in our previous report.[11b] In short, path (i) proceeds through the nucleophilic attack of the carbanion generated by deprotonation at the α-carbon of the aldehyde to C_{60}, subsequent oxidation and addition of the alkoxide to the carbonyl group on the side chain

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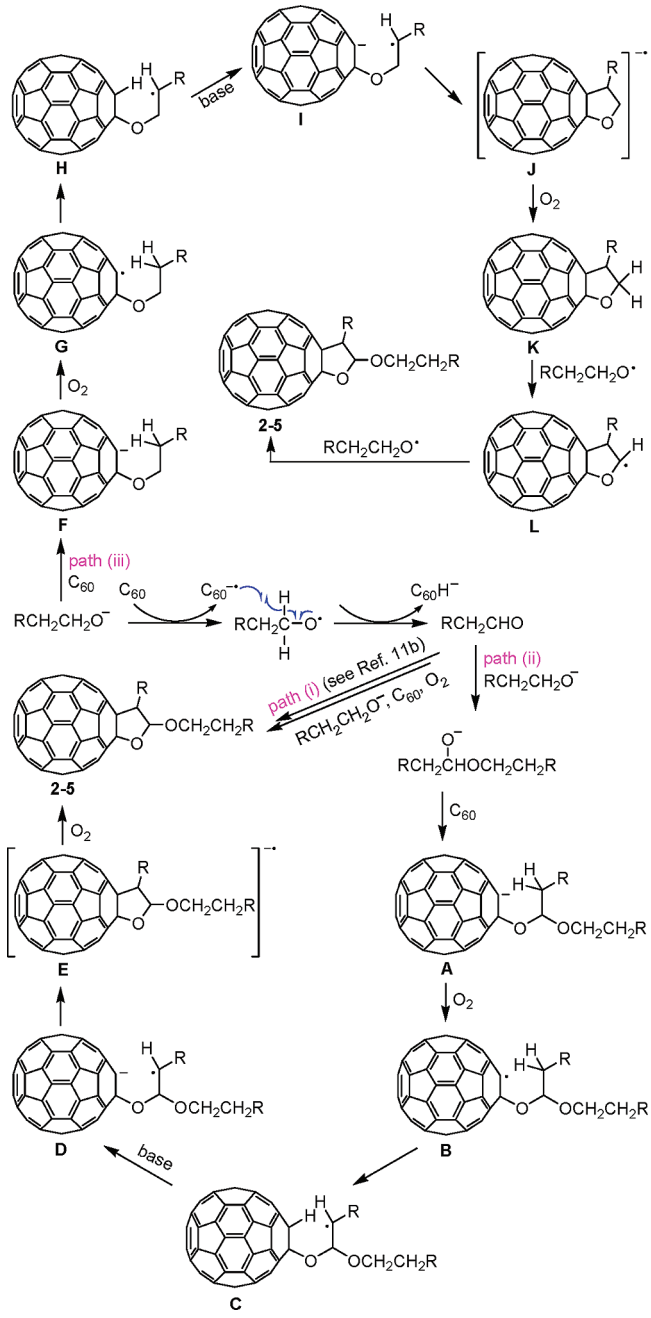
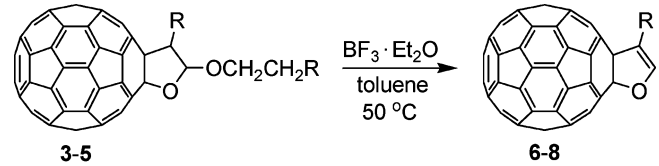
SCHEME 3. Possible Reaction Mechanism for the Formation of Products 2−5



of the formed radical species, and final ring closure via an intramolecular nucleophilic addition and oxidation.[11b] Alternatively, the reaction might occur through path (ii) to generate products **2**−**5**. The hemiacetal intermediate, formed by the addition of the alkoxide to the corresponding aldehyde, reacts with C_{60} to afford fullerenyl anion **A**. Oxidation of intermediate **A** gives fullerenyl radical **B**, and subsequent intramolecular hydrogen abstraction and deprotonation generates radical anion **D**. Intramolecular cyclization of intermediate **D** and oxidation afford the final products **2**−**5**. The third possible mechanism for the formation of products **2**−**5** involving alkoxides but no aldehydes is shown as path (iii) in Scheme 3. Nucleophilic addition of the alkoxide to C_{60} followed by oxidation furnishes fullerenyl radical **G**. Intramolecular hydrogen abstraction of radical **G** and subsequent deprotonation give radical anion **I**,

SCHEME 4. Conversion of 3−5 to 6−8 Promoted by $BF_3 \cdot Et_2O$ at 50 °C



3, **6**: R = CH_3; **4**, **7**: R = CH_2CH_3; **5**, **8**: R = Ph

which undergoes intramolecular cyclization and oxidation to afford intermediate **K**. Hydrogen abstraction presumably by $RCH_2CH_2O^•$ at the methylene moiety next to the oxygen atom of intermediate **K** produces radical **L**, which then couples with $RCH_2CH_2O^•$ to generate products **2**−**5**. The suggested six steps giving products **2**−**5** in path (ii) are similar to the first six steps affording intermediate **K** in path (iii). The failure to observe and isolate intermediate **K** from the reaction of C_{60} with alkoxides at the early stage as well as at the end of reaction indicates that the reaction of C_{60} with alkoxides should proceed through path (i) rather than path (ii) and path (iii). Furthermore, the stronger nucleophilicity for a carboanion than that for an oxygen nucleophile such as an alkoxide or hemiacetal anion in nonprotonic solvents (toluene in the current work) also supports that the reaction preferably occurs via path (i).

Further transformation of fullerene products gains more and more attention for the preparation of new fullerene derivatives.[1−6,11a,14] Significantly, the challenging synthesis of $H_2@C_{60}$ and $H_2@C_{70}$ was achieved by Komatsu, Murata, and co-workers who closed the 13-membered ring orifice of the corresponding hydrogen-encapsulated open-cage fullerenes by four-step organic reactions.[14a−c] The Gan group prepared azafullerene derivatives with peroxide addends by addition of hydroxyl amine to cage-opened fullerene derivatives, subsequent PCl_5-induced rearrangement, and final treatment with basic alumina or amines.[14d] We therefore investigated the subsequent derivatization of products **2**−**5** in order to obtain other valuable fullerene derivatives.

After extensive screening of the reaction conditions, it was found that boron trifluoride etherate ($BF_3 \cdot Et_2O$) could efficiently convert compounds *cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, and *trans*-**5** to C_{60}-fused dihydrofuran derivatives **6**−**8** with the apparent loss of RCH_2CH_2OH at 50 °C (Scheme 4).

The reaction times and yields for the reaction of both *cis* and *trans* isomers of compounds **3**−**5** with 100 equiv of $BF_3 \cdot Et_2O$ at 50 °C affording products **6**−**8** are listed in Table 3. As can be seen from Table 3, the stereochemistry of the reactants had little influence on the product yields; both *cis* and *trans* isomers gave the identical product in nearly the same

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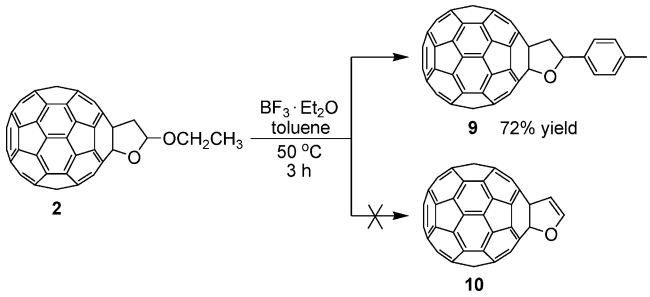
TABLE 3. Reaction Times and Yields for the Conversion of 3−5 to 6−8 Promoted by $BF_3 \cdot Et_2O$ at 50 °C

substrate	reaction time (h)	product	yield (%)
cis-**3**	1	**6**	81
trans-**3**	1	**6**	79
cis-**4**	1	**7**	84
trans-**4**	1	**7**	83
cis-**5**	3	**8**	80
trans-**5**	3	**8**	81

SCHEME 5. Conversion of 2 to 9 Promoted by $BF_3 \cdot Et_2O$ at 50 °C



yields (79−84%). For example, the *cis*-**3** and *trans*-**3** afforded product **6** in 81% and 79% yields, respectively.

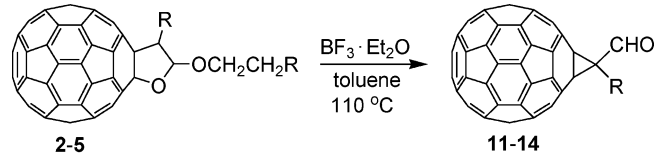
Products **6** and **8** are known compounds, and their identities were confirmed by comparison of their spectral data with the reported ones.[11a] Product **7** showed ^{13}C NMR and UV−vis spectra similar to those of products **6** and **8**.[11a] In the ^{13}C NMR spectrum of product **7**, there were 29 lines including two half-intensity ones in the 134−148 ppm range for the 58 sp^2-carbons of the C_{60} skeleton and two peaks (74.61 and 100.50 ppm) for the two sp^3-carbons of the C_{60} moiety, consistent with its C_s molecular symmetry.

A carbonyl group was usually attached to the olefinic carbons in the reported C_{60}-fused dihydrofurans, which were commonly prepared from the reaction of C_{60} with β-keto esters or β-diketones in the presence of a base[15] or a metal oxidant.[16] However, alkyl- or aryl-substituted C_{60}-fused dihydrofurans have been much less investigated in the literature.[11a,16b] Our current protocol of synthesizing the 3-alky- and 3-aryl-substituted C_{60}-fused dihydrofurans requires two steps starting from C_{60}, complementing our previous methodology, which demanded three steps beginning with C_{60} via the synthesis of C_{60}-fused lactones,[17] followed by reduction with DIBAL and then acid-promoted dehydration.[11a]

To our surprise, treatment of compound **2** with $BF_3 \cdot Et_2O$ in toluene produced tolyl-substituted tetrahydrofuran **9**, rather than the corresponding C_{60}-fused dihydrofuran product **10** (Scheme 5).

The similarity of the ^{13}C NMR patterns in the 134−155 ppm range for the sp^2-carbons of the C_{60} moiety between product **2** and product **9** together with the close chemical shifts for the two sp^3-carbons of the C_{60} cage (66.71 and 98.41 ppm for **2** vs 68.31 and 97.88 ppm for **9**) indicates that the skeleton of product **9** is the same as that of its precursor **2**. However, in the ^1H NMR spectrum of product **9** the methine proton on the tetrahydrofuran ring showed much larger coupling constants (11.4 and 3.9 Hz) due to the lack of the acetal moiety, dramatically larger than the corresponding values (3.3 and 1.2 Hz) in compound **2**.

SCHEME 6. Conversion of 2−5 to 11−14 Promoted by $BF_3 \cdot Et_2O$ at 110 °C



2, **11**: R = H; **3**, **12**: R = CH_3; **4**, **13**: R = CH_2CH_3; **5**, **14**: R = Ph

TABLE 4. Reaction Times and Yields for the Conversion of 2−5 to 11−14 Promoted by $BF_3 \cdot Et_2O$ at 110 °C

substrate	reaction time (h)	product	yield (%)
2	1	**11**	33
cis-**3**	1	**12**	84
trans-**3**	1	**12**	74
cis-**4**	1	**13**	82
trans-**4**	1	**13**	79
cis-**5**	3	**14**	33
trans-**5**	3	**14**	28

Interestingly, when the reaction temperature was increased to the refluxing temperature of toluene, the reaction of compounds **2**−**5** with $BF_3 \cdot Et_2O$ gave another type of products, that is, methanofullerenes **11**−**14** (Scheme 6).

The reaction times and yields for the reaction of **2**, *cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, and *trans*-**5** with 200 equiv of $BF_3 \cdot Et_2O$ at 110 °C affording products **11**−**14** are listed in Table 4.

Both *cis* and *trans* isomers gave the same product in nearly the same yields. For example, the *cis*-**4** and *trans*-**4** isomers afforded product **13** in 82% and 79% yields, respectively. It should be noted that the competing product **9** was also isolated in 48% yield from the reaction of **2** with $BF_3 \cdot Et_2O$ at 110 °C. Products **6**−**8** were also formed from the reaction of *cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, and *trans*-**5** with $BF_3 \cdot Et_2O$ and isolated in 14%, 15%, 14%, 16%, 65%, and 68% yields, respectively. The yields for products **11**−**14** could not be improved by increasing the reaction temperature or prolonging the reaction time for the reaction of compounds **2**−**5** with $BF_3 \cdot Et_2O$ at 110 °C.

Full spectral characterization including HRMS, ^1H NMR, ^{13}C NMR, UV−vis, and IR spectra had also been carried out for methanofullerenes **11**−**14**. The δ_H at ca. 10 ppm, δ_C at ca. 190 ppm, and IR absorption at ca. 1720 cm^{-1} clearly demonstrated the existence of the formyl group. The observation of no more than 27 peaks for the 58 sp^2-carbons of the C_{60} skeleton and one peak at ca. 75 ppm for the two sp^3-carbons of the C_{60} cage agrees well with its C_s molecular symmetry.

Methanofullerenes **11**−**14** are expected to have wide application in further transformations due to the formyl group.[18] Product **13** has been prepared by the reaction of C_{60} with an α-formyl sulfonium ylide.[18a] However, the attempted synthesis of a

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(16) (a) Li, C.; Zhang, D.; Zhang, X.; Wu, S.; Gao, X. *Org. Biomol. Chem.* **2004**, *2*, 3464. (b) Wang, G.-W.; Li, F.-B. *Org. Biomol. Chem.* **2005**, *3*, 794. (c) Chen, X.; Wang, G.-W.; Murata, Y.; Komatsu, K. *Chin. Chem. Lett.* **2005**, *16*, 1327.

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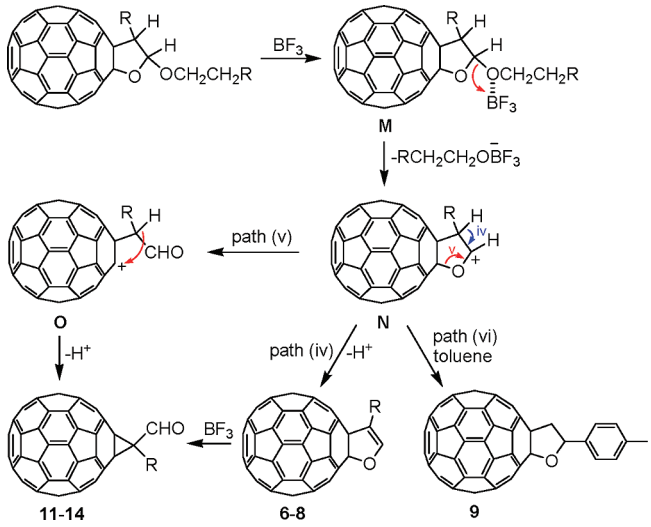
SCHEME 7. Plausible Reaction Mechanism for the Formation of Products 6−9 and 11−14



methanofullerene with the benzyl group replacing the ethyl group in product **13** was unsuccessful. The failure was ascribed to the steric repulsion between the C_{60} core and the benzyl group and/or due to the formation of the less reactive dimethylsulfonium enolate. In comparison, methanofullerene **14** having a phenyl group, which should be more sterically demanding than the benzyl group, could be obtained successfully by our protocol.

Even though the exact pathways for the formation of products **6**−**9** and **11**−**14** are not clear right now, a possible mechanism for their formation is shown in Scheme 7.

The BF_3-induced C−O bond cleavage of the epoxy ring[14f,19] and $B(C_6F_5)_3$-induced O−O bond cleavage of the *tert*-butylperoxy group[20] are known in fullerene chemistry. Similarly, BF_3 can complex with the oxygen atom of the RCH_2CH_2O moiety (complex **M**) and then induce the C−O bond heterocleavage to give cationic intermediate **N**. Proton elimination from intermediate **N** via path (iv) (at a lower temperature of 50 °C) results in C_{60}-fused dihydrofurans **6**−**8**. The C−O bond rupture via path (v) (at a higher temperature of 110 °C) affords fullerenyl cation **O** with a formyl group. Subsequent cyclization accompanied by the loss of H^+ affords methanofullerenes **11**−**14**. Alternatively, methanofullerenes could also be generated by first formation of C_{60}-fused dihydrofurans, followed by BF_3-induced rearrangement. This possibility was evidenced by the fact that the amount of formed C_{60}-fused dihydrofurans at the early stage of the reactions at 110 °C was significantly more than that at the end of the reactions. This pathway was further supported by a control experiment, which showed that C_{60}-fused dihydrofuran **6** could be converted to methanofullerene **12** in the presence of 200 equiv of $BF_3 \cdot Et_2O$ at 110 °C. We believe that the two parallel pathways leading to methanofullerenes **11**−**14** might operate at the same time. For R = H, intermediate **N** preferably reacts with toluene (the solvent) via path (vi) to give product **9** rather than the corresponding C_{60}-fused dihydrofuran **10**. This phenomenon might be ascribed to the fact that toluene can attack intermediate **N** much easier for R = H because of less steric hindrance and that it is more difficult to form product **10** having no substituent than products **6**−**8** bearing an alky or aryl substituent. Experimentally, product **9** was obtained exclusively at lower temperature and was still a major product at higher temperature. The fact that the *cis* and *trans* stereochemistries of *cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, and *trans*-**5** did not affect the formation rates and yields of products **6**−**8** and **12**−**14** strongly substantiated the generation of the same carbocation **N**, of which the cationic carbon had a sp^2-hybridization and trigonal planar geometry and would not have any influence on the subsequent steps.

Conclusion

The reaction of C_{60} with freshly prepared RCH_2CH_2ONa/RCH_2CH_2OH (R = H, Me, Et, Ph) in anhydrous toluene in the presence of air unexpectedly afforded fullerene products **2**−**5**, which contained a C_{60}-fused tetrahydrofuran ring skeleton and an acetal moiety. This novel type of fullerene products is different from that of our previously reported C_{60}-fused 1,3-dioxolane derivative that was generated from the reaction of C_{60} with $PhCH_2ONa/PhCH_2OH$, indicating that the reactions with two different types of alkoxides proceeded in different reaction pathways. Depending on the reaction conditions and molecular structures, products **2**−**5** could be further converted to C_{60}-fused dihydrofurans **6**−**8**, tolyl-substituted C_{60}-fused tetrahydrofuran **9**, and methanofullerenes **11**−**14** bearing a formyl group in the presence of boron trifluoride etherate. Possible reaction mechanisms for the formation of these different fullerene products **6**−**9** and **11**−**14** are proposed.

Experimental Section

Synthesis of Products 2−5 from the Reaction of C_{60} with RCH_2CH_2ONa/RCH_2CH_2OH in the Presence of Air. A mixture of C_{60} (50.4 mg, 0.07 mmol) and RCH_2CH_2ONa/RCH_2CH_2OH (1.4 mL, 0.7 mmol RCH_2CH_2ONa, freshly prepared by treating 10 mL of RCH_2CH_2OH with 115.0 mg of sodium) was completely dissolved in anhydrous toluene (35 mL) with the aid of sonication. After stirring at room temperature for the desired time, the reaction mixture was filtered through a silica gel plug in order to remove the unreacted sodium alkoxide and any other polar material. Then the solvent was evaporated in vacuo, and the residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} and compound **2** (*cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, *trans*-**5**).

2: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 1.45 (t, J = 7.1 Hz, 3H), 3.88−3.99 (m, 3H), 4.32 (dq, J = 9.5, 7.1 Hz, 1H), 6.15 (dd, J = 3.3, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 14.72, 48.22, 63.00, 66.71 (sp^3-C of C_{60}), 98.41 (sp^3-C of C_{60}), 102.68, 134.79, 136.51, 137.11, 137.31, 138.96, 139.12, 139.44, 139.53, 141.03, 141.12, 141.35, 141.46 (2C), 141.66 (4C), 141.77, 142.02 (2C), 142.08 (2C), 142.16 (2C), 142.40 (2C), 143.83, 144.13, 144.21 (2C), 144.59 (2C), 144.66 (3C), 144.70, 144.73, 144.77, 144.82 (2C), 145.11, 145.17, 145.38, 145.41, 145.51 (3C), 145.63, 145.74, 145.78, 145.83, 145.86, 146.86, 147.48, 148.32, 150.71, 154.93, 155.58; FT-IR ν/cm^{-1} (KBr) 2968, 2920, 1511, 1463, 1430, 1367, 1315, 1211, 1170, 1101, 1038, 1017, 991, 937, 858, 766, 594, 575, 554, 526, 504, 477; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 253 (5.00), 314 (4.36), 427 (3.22), 696 (2.38); HRMS (ESI) calcd for $C_{64}H_8NaO_2$ $[M + Na]^+$ 831.0422, found 831.0416.

cis-**3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (t, J = 7.5 Hz, 3H), 1.80−1.92 (m, 2H), 1.89 (d, J = 7.0 Hz, 3H) 3.82 (dt, J = 9.5, 6.5 Hz, 1H), 4.09 (dq, J = 7.0, 3.9 Hz, 1H), 4.28 (dt, J = 9.5, 6.5 Hz, 1H), 5.97 (d, J = 3.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 11.03,

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12.94, 23.07, 53.37, 69.83, 71.66 (sp^3-C of C_{60}), 99.41 (sp^3-C of C_{60}), 105.51, 135.29, 137.87, 138.07, 138.18, 139.64, 139.74, 139.87, 140.25, 141.67, 141.71, 142.00, 142.15, 142.21, 142.38 (2C), 142.40 (2C), 142.50, 142.55, 142.76, 142.79 (2C), 142.85 (2C), 143.06, 143.10, 144.45, 144.86 (2C), 144.99, 145.22, 145.30 (2C), 145.37 (3C), 145.39, 145.55, 145.78, 145.81, 146.05 (2C), 146.11, 146.17, 146.20, 146.23, 146.38, 146.39, 146.48, 146.52, 146.55, 146.78, 147.53, 148.19, 148.99, 152.00, 153.35, 156.55; FT-IR ν/cm^{-1} (KBr) 2955, 2869, 1451, 1428, 1180, 1103, 1074, 998, 966, 943, 765, 592, 575, 553, 526, 499, 476; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.01), 313 (4.51), 427 (3.38), 696 (2.40); HRMS (ESI) calcd for $C_{66}H_{12}NaO_2$ $[M + Na]^+$ 859.0735, found 859.0719.

trans-**3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, J = 7.4 Hz, 3H), 1.87 (sextet, J = 7.1 Hz, 2H), 1.96 (d, J = 7.2 Hz, 3H), 3.85 (dt, J = 9.4, 6.7 Hz, 1H), 4.14 (q, J = 7.2 Hz, 1H), 4.25 (dt, J = 9.4, 6.7 Hz, 1H), 5.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 10.50, 18.46, 22.60, 52.06, 69.57, 70.96 (sp^3-C of C_{60}), 98.09 (sp^3-C of C_{60}), 109.78, 136.18, 136.46, 137.30, 137.91, 139.00, 139.07, 139.25, 139.39, 140.88, 141.03, 141.34, 141.37, 141.44, 141.62 (3C), 141.70, 141.72, 141.76, 142.00, 142.03, 142.08, 142.12, 142.18, 142.36, 142.43, 143.84, 144.14, 144.18 (2C), 144.51, 144.58, 144.60, 144.67 (3C), 144.70, 144.77, 144.92, 145.10 (2C), 145.33 (3C), 145.45, 145.49, 145.53, 145.55, 145.75 (2C), 145.85, 145.88, 146.86, 147.47, 148.95, 150.44, 152.99, 155.64; FT-IR ν/cm^{-1} (KBr) 2921, 1452, 1426, 1174, 1102, 998, 953, 765, 596, 574, 524, 477; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.00), 312 (4.51), 428 (3.36), 694 (2.38); HRMS (ESI) calcd for $C_{66}H_{12}NaO_2$ $[M + Na]^+$ 859.0735, found 859.0723.

cis-**4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (t, J = 7.4 Hz, 3H), 1.39 (t, J = 7.4 Hz, 3H), 1.58 (sextet, J = 7.4 Hz, 2H), 1.77−1.86 (m, 2H), 2.33−2.46 (m, 2H), 3.84−3.94 (m, 2H), 4.32 (dt, J = 9.6, 6.3 Hz, 1H), 6.07 (d, J = 3.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 12.88, 13.96, 19.41, 22.18, 31.59, 60.07, 67.75, 71.07 (sp^3-C of C_{60}), 99.41 (sp^3-C of C_{60}), 104.04, 135.09, 137.62, 137.68, 137.79, 139.40, 139.50, 139.53, 139.90, 141.40, 141.45, 141.71, 141.90, 141.94, 142.13 (2C), 142.16 (2C), 142.25, 142.31, 142.52, 142.54 (2C), 142.61 (2C), 142.81, 142.87, 144.21, 144.62 (2C), 144.75, 144.97, 145.04, 145.08, 145.10 (2C), 145.12 (2C), 145.32, 145.60, 145.65, 145.80 (2C), 145.83, 145.92, 145.95, 145.97, 146.12, 146.15, 146.24, 146.26, 146.30, 146.46, 147.27, 147.93, 148.84, 151.70, 153.39, 156.36; FT-IR ν/cm^{-1} (KBr) 2955, 2925, 2868, 1459, 1428, 1377, 1341, 1304, 1177, 1152, 1137, 1104, 1082, 995, 946, 894, 766, 576, 563, 553, 527, 479; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (4.89), 313 (4.53), 428 (3.40), 695 (2.47); HRMS (ESI) calcd for $C_{68}H_{16}NaO_2$ $[M + Na]^+$ 887.1048, found 887.1040.

trans-**4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, J = 7.4 Hz, 3H), 1.44 (t, J = 7.4 Hz, 3H), 1.60 (sextet, J = 7.2 Hz, 2H), 1.84 (penta, J = 7.1 Hz, 2H), 2.42 (penta, J = 7.3 Hz, 2H), 3.86−3.95 (m, 2H), 4.29 (dt, J = 9.0, 7.2 Hz, 1H), 5.97 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 13.20, 13.91, 19.26, 26.54, 31.50, 59.61, 67.98, 71.52 (sp^3-C of C_{60}), 98.41 (sp^3-C of C_{60}), 107.90, 136.33, 136.71, 137.72, 138.31, 139.37, 139.40, 139.48, 139.70, 141.21, 141.37, 141.66, 141.69, 141.80, 141.96, 141.98, 142.02, 142.09 (3C), 142.37, 142.39, 142.45, 142.48, 142.55, 142.71, 142.80, 144.20, 144.51, 144.55 (2C), 144.84, 144.88, 145.00 (2C), 145.04 (2C), 145.13, 145.16, 145.22, 145.49, 145.62, 145.71 (3C), 145.84, 145.88 (2C), 145.90, 146.12, 146.15, 146.19, 146.25, 147.25, 147.86, 149.14, 150.87, 153.47, 156.32; FT-IR ν/cm^{-1} (KBr) 2955, 2925, 2866, 1459, 1428, 1378, 1358, 1171, 1109, 1094, 998, 944, 840, 766, 575, 556, 527, 480; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (4.91), 313 (4.52), 428 (3.37), 691 (2.42); HRMS (ESI) calcd for $C_{68}H_{16}NaO_2$ $[M + Na]^+$ 887.1048, found 887.1056.

cis-**5**: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 3.19 (t, J = 6.4 Hz, 2H), 4.16 (dt, J = 9.4, 6.4 Hz, 1H), 4.69 (dt, J = 9.4, 6.4 Hz, 1H), 5.10 (d, J = 3.7 Hz, 1H), 6.14 (d, J = 3.7 Hz, 1H), 7.19−7.37 (m, 8H), 7.76−7.79 (m, 2H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 36.00, 64.43, 68.87, 71.96 (sp^3-C of C_{60}), 98.35 (sp^3-C of C_{60}), 104.40, 126.24, 127.86 (3C), 128.29 (2C), 128.77 (2C), 131.40 (2C), 133.45, 134.58, 137.32, 137.36, 137.41, 138.50, 139.09 (2C), 139.16, 139.43, 140.95, 141.27, 141.39, 141.62, 141.65, 141.74, 141.75, 141.78, 141.80, 141.93, 141.95, 141.99, 142.22 (4C), 142.42, 142.44, 143.82, 144.18, 144.23, 144.38, 144.51, 144.60, 144.77 (4C), 144.87, 145.08, 145.20, 145.31, 145.37, 145.45, 145.52, 145.63 (3C), 145.73, 145.78, 145.84, 145.93, 145.99 (2C), 146.91, 147.58, 148.32, 150.80, 152.10, 155.19; FT-IR ν/cm^{-1} (KBr) 2918, 2850, 1494, 1453, 1428, 1181, 1127, 1098, 996, 942, 860, 745, 696, 576, 553, 543, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (4.92), 314 (4.46), 427 (3.28), 693 (2.31); HRMS (ESI) calcd for $C_{76}H_{16}NaO_2$ $[M + Na]^+$ 983.1048, found 983.1050.

trans-**5**: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 3.13 (t, J = 6.6 Hz, 2H), 4.10 (dt, J = 9.3, 6.6 Hz, 1H), 4.55 (dt, J = 9.3, 6.6 Hz, 1H), 5.22 (s, 1H), 6.13 (s, 1H), 7.13−7.36 (m, 6H), 7.45 (t, J = 7.5 Hz, 2H), 7.86 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 36.38, 64.81, 69.03, 73.35 (sp^3-C of C_{60}), 99.11 (sp^3-C of C_{60}), 109.16, 126.66, 128.14, 128.64 (2C), 128.68 (2C), 129.26 (2C), 129.43 (2C), 136.72, 136.90, 137.81, 138.86, 138.92, 139.37, 139.50, 139.70, 139.73, 139.93, 141.57, 141.89 (3C), 142.04, 142.09, 142.23 (2C), 142.33, 142.37 (2C), 142.64, 142.69, 142.71, 142.76, 142.78, 142.90, 142.95, 144.40, 144.65, 144.77, 144.79, 145.03, 145.13 (2C), 145.18, 145.23, 145.24, 145.27, 145.30 (3C), 145.69, 145.77 (2C), 145.98, 146.01, 146.08, 146.15 (2C), 146.23, 146.39, 146.40, 146.51, 147.53, 148.12, 148.70, 150.48, 154.08, 155.76; FT-IR ν/cm^{-1} (KBr) 2918, 2862, 1512, 1493, 1452, 1428, 1355, 1186, 1169, 1093, 1054, 1013, 987, 939, 839, 746, 697, 575, 563, 553, 525, 490; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (4.98), 314 (4.51), 427 (3.31), 693 (2.35); HRMS (ESI) calcd for $C_{76}H_{16}NaO_2$ $[M + Na]^+$ 983.1048, found 983.1045.

Synthesis of Products 2−5 from the Reaction of C_{60} with RCH_2CH_2ONa/RCH_2CH_2OH and RCH_2CHO in the Presence of Air. A mixture of C_{60} (50.4 mg, 0.07 mmol) and RCH_2CH_2ONa/RCH_2CH_2OH (1.4 mL, 0.7 mmol RCH_2CH_2ONa, freshly prepared by treating 10 mL of RCH_2CH_2OH with 115.0 mg of sodium) was completely dissolved in anhydrous toluene (35 mL) with the aid of sonication. Then RCH_2CHO (0.07 mmol) was added. After stirring at room temperature for the desired time, the same workup as above gave the unreacted C_{60} and compound **2** (*cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, *trans*-**5**).

Conversion of Compounds 3−5 to Products 6−8 in the Presence of Boron Trifluoride Etherate at 50 °C. C_{60}-fused tetrahydrofuran *cis*-**3** (*trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, or *trans*-**5**) (0.015 mmol) was dissolved in toluene (7 mL) with the aid of sonication. Then 1.5 mmol of boron trifluoride etherate was added. After stirring at 50 °C for the desired time, the reaction mixture was filtered through a silica gel plug. Then the solvent was evaporated in vacuo, and the residue was separated on a silica gel column with carbon disulfide as the eluent to give compound **6** (**7** or **8**).

7: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 1.54 (t, J = 7.4 Hz, 3H), 2.75 (dq, J = 7.2, 1.8 Hz, 2H), 6.96 (t, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 2C unless indicated) δ 12.36 (1C), 19.21 (1C), 74.61 (1C, sp^3-C of C_{60}), 100.50 (1C, sp^3-C of C_{60}), 117.04 (1C), 134.80, 135.82, 138.51 (1C), 138.61, 139.27, 140.42, 140.75, 140.94, 141.07, 141.11, 141.47, 141.50 (4C), 141.72, 143.17, 143.18, 143.84, 143.90, 144.00, 144.15, 144.41, 144.50, 144.68, 144.76, 144.86, 144.90, 144.94, 145.03, 146.07 (1C), 146.81 (1C), 147.95; FT-IR ν/cm^{-1} (KBr) 2959, 2919, 1666, 1629, 1429, 1182, 1121, 1051, 1006, 980, 942, 901, 846, 767, 596, 574, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.02), 314 (4.51), 426 (3.35), 691 (2.35); HRMS (ESI) calcd for $C_{64}H_6NaO$ $[M + Na]^+$ 813.0316, found 813.0308.

Conversion of 2 to 9 Promoted by $BF_3 \cdot Et_2O$ at 50 °C. Compound **2** (12.4 mg, 0.015 mmol) was dissolved in toluene (7

mL) with the aid of ultrasonication. Then boron trifluoride etherate (200 μL, 1.5 mmol) was added. After stirring at 50 °C for 3 h, the reaction mixture was filtered through a silica gel plug. Then the solvent was evaporated in vacuo, and the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give the crude product along with recovered compound **2** (1.5 mg, 12%). Further HPLC purification on a Cosmosil Buckyprep column (4.6 mm × 250 mm) gave pure compound **9** (9.3 mg, 72%). ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 2.47 (s, 3H), 3.83 (dd, J = 12.0, 11.4 Hz, 1H), 4.10 (dd, J = 12.0, 3.9 Hz, 1H), 6.24 (dd, J = 11.4, 3.9 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 20.99, 50.46, 68.31 (sp^3-C of C_{60}), 78.27, 97.88 (sp^3-C of C_{60}), 126.13 (2C), 128.99 (2C), 134.48, 135.33, 136.07, 136.93, 137.48, 137.52, 138.91, 139.25, 139.39, 139.51, 140.66, 141.08, 141.14, 141.43, 141.48, 141.52 (2C), 141.54, 141.65 (2C), 141.84, 141.95, 141.98 (2C), 142.02, 142.06, 142.21, 142.25, 143.75, 143.93 (2C), 144.07, 144.20, 144.43, 144.49, 144.52 (2C), 144.55, 144.62 (3C), 144.77, 144.90, 145.18, 145.29, 145.38 (2C), 145.43 (2C), 145.56, 145.64 (2C), 145.66, 145.73, 146.73, 147.33, 148.15, 149.47, 154.22, 154.92; FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1512, 1459, 1428, 1374, 1305, 1264, 1175, 1110, 1016, 995, 811, 770, 600, 565, 525; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 254 (5.08), 314 (4.61), 428 (3.45), 691 (2.36); HRMS (ESI) calcd for $C_{69}H_{10}NaO$ $[M + Na]^+$ 877.0629, found 877.0617.

Conversion of Compounds 2−5 to Products 11−14 in the Presence of Boron Trifluoride Etherate at 110 °C. Compound **2** (*cis*-**3**, *trans*-**3**, *cis*-**4**, *trans*-**4**, *cis*-**5**, or *trans*-**5**) (0.015 mmol) was dissolved in toluene (7 mL) with the aid of sonication. Then 3.0 mmol of boron trifluoride etherate was added. After stirring at the refluxing temperature (with an oil bath of 120 °C) for the desired time, the reaction mixture was filtered through a silica gel plug. Then the solvent was evaporated in vacuo, and the residue was separated on a silica gel column with carbon disulfide as the eluent to give product **9** (**6**, **7**, or **8**) and then product **11** (**12**, **13**, or **14**).

11: ^{1}H NMR (300 MHz, $CS_2/C_6D_4Cl_2$) δ 4.55 (d, J = 5.0 Hz, 1H), 10.26 (d, J = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CS_2/C_6D_4Cl_2$, all 2C unless indicated) δ 44.96 (1C), 71.09 (sp^3-C of C_{60}), 137.19, 139.32, 141.78 (4C), 142.40, 142.61, 142.72, 143.02, 143.57 (8C), 143.71, 144.33, 144.42, 145.13 (1C), 145.18 (4C), 145.21 (1C), 145.25 (4C), 145.31, 145.44, 145.75, 145.82 (6C), 145.86, 146.03, 148.59, 190.71 (1C, CHO); FT-IR ν/cm^{-1} (KBr) 2921, 2850, 1718, 1540, 1460, 1428, 1315, 1184, 1116, 1063, 797, 709, 574, 526, 494; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.09), 326 (4.54), 427 (3.37), 690 (2.17); HRMS (MALDI FT-ICR) calcd for $C_{62}H_2O$ $[M]^-$ 762.0106, found 762.0098.

12: ^{1}H NMR (300 MHz, $CS_2/C_6D_4Cl_2$) δ 2.20 (s, 3H), 10.42 (s, 1H); ^{13}C NMR (75 MHz, $CS_2/C_6D_4Cl_2$ with Cr(acac)$_3$ as relaxation reagent, all 2C unless indicated) δ 11.70 (1C), 45.43 (1C), 76.18 (sp^3-C of C_{60}), 135.40, 135.41, 138.20, 138.44, 141.35, 141.45, 141.86, 142.39, 143.27 (6C), 143.34 (1C), 143.37, 143.48 (1C), 144.01, 144.08, 144.71, 144.88 (1C), 144.93 (6C), 144.97 (1C), 145.02, 145.33, 145.45, 145.49, 145.54 (4C), 145.56, 146.05, 147.09, 193.38 (1C, CHO); FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1716, 1507, 1427, 1380, 1261, 1184, 1084, 1039, 951, 868, 797, 736, 706, 573, 557, 525; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.09), 327 (4.56), 429 (3.40), 688 (2.26); HRMS (MALDI FT-ICR) calcd for $C_{63}H_4O$ $[M]^-$ 776.0262, found 776.0268.

14: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 7.51−7.60 (m, 3H), 7.91 (d, J = 7.5 Hz, 2H), 10.45 (s, 1H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 2C unless indicated) δ 57.27 (1C), 74.11 (sp^3-C of C_{60}), 128.33, 128.74 (1C), 129.57 (1C), 131.98, 137.52, 137.90, 140.19, 140.38, 140.95, 141.07, 141.26, 141.35, 142.09, 142.15 (3C), 142.18, 142.26, 142.38 (1C), 142.90, 143.08, 143.63 (1C), 143.68, 143.78, 143.84, 143.91 (5C), 143.95, 144.32, 144.39 (4C), 144.42, 144.55, 144.59, 145.55, 189.08 (1C, CHO); FT-IR ν/cm^{-1} (KBr) 2923, 2853, 1722, 1507, 1461, 1427, 1377, 1261, 1183, 1094, 1024, 801, 698, 575, 525; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.09), 327 (4.58), 428 (3.38), 691 (2.29); HRMS (MALDI FT-ICR) calcd for $C_{68}H_6O$ $[M]^-$ 838.0419, found 838.0411.

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Supporting Information Available: NMR spectra of compounds **2**−**9**, **11**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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