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Synthesis of [60]Fullerene Acetals and Ketals: Reaction of [60]Fullerene with Aldehydes/Ketones and Alkoxides

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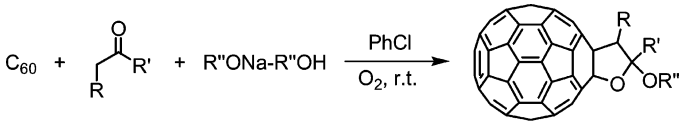

The reaction of C_{60} with propionaldehyde (butyraldehyde or phenylacetaldehyde) and MeONa−MeOH or EtONa−EtOH in anhydrous chlorobenzene in the presence of air at room temperature unexpectedly gave rare fullerene acetals **2aa**−**cb**, while the reaction of C_{60} with acetone (acetophenone, cyclohexanone, or cyclopentanone) and MeONa−MeOH or EtONa−EtOH under the same conditions afforded the uncommon fullerene ketals **4aa**−**db**. A possible reaction mechanism for the formation of the fullerene acetals and ketals is proposed based on further experimental results.

Introduction

Many chemical reactions have been discovered for the functionalization of fullerenes.[1] Although numerous fullerene products with wide structural diversities are known, fullerene hemiacetals/acetals and hemiketals/ketals are relatively rare.[2] In most cases, fullerene derivatives were employed to further transform into fullerene acetals and ketals. In our preceding paper, fullerene hemiacetals and hemiketals were obtained from the reaction of C_{60}-fused lactones with diisobutylaluminum hydride and methylmagnesium bromide, respectively.[3] Fullerene epoxides $C_{60}O_n$ ($n = 1, 2$) reacted with benzaldehyde derivatives in the presence of *N*-(1-phenethyl)-2-cyanopyridinium hexafluoroantimonate to give fullerene acetals.[2c] Gan and co-workers reported that the peroxo O−O bond of vicinal hydroxy chloride $C_{60}Cl(OH)(OO^tBu)_4$ was cleaved by aluminum chloride to form both [5,6]- and [6,6]-fullerene hemiketals.[2d] They also described the reaction of a cage-opened fullerendione $C_{60}O_2(OO^tBu)_4$ with oxygen nucleophiles in the presence of $BF_3{\cdot}Et_2O$ to form fullerene hemiketal/ketal derivatives through coupling of the two carbonyl groups.[2e] Chiang et al. obtained the evidence of hemiketals incorporated onto the fullerene ball structure skeleton in the structures of polyhydroxylated fullerene derivatives (fullerols) that were prepared from the aqueous acid reaction of [60]fullerene (C_{60}) in the presence of sulfuric acid and nitric acid, even though the exact structures of the fullerols were unknown.[2a] Wang et al. reported the only example for the direct synthesis of a fullerene acetal derivative without structural obscurity from the reaction of C_{60} itself with $PhCH_2ONa$−$PhCH_2OH$ under aerobic conditions.[2b]

Aldehydes and ketones are usually first converted to azomethine ylides[1,4] or diazo compounds,[1] which then react with fullerenes to obtain fullerene derivatives. Even though 1,3-dicarbonyl compounds, such as malonate esters,[5] β-keto esters,[5d,6] and β-diketones,[5d,6,7] were utilized in the functionalization of C_{60}, the direct reactions of aldehydes and ketones with C_{60} have

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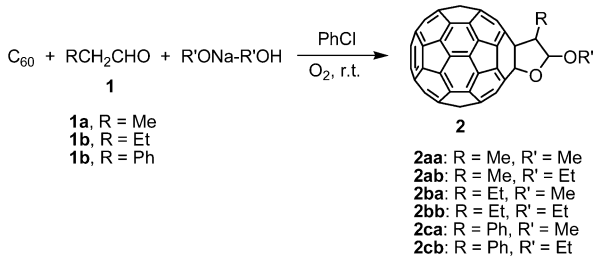
SCHEME 1. Reaction of C_{60} with Aldehydes and Alkoxides



been seldom explored. Previously, we reported the reactions of aromatic methyl ketones with C_{60} to give C_{60}-fused tetrahydrofurans and/or methanofullerenes under solvent-free mechanical milling conditions[5d] and mediated by $Cu(OAc)_2 \cdot H_2O$ or $Mn(OAc)_3 \cdot 3H_2O$.[6b] In this paper, we report that combinations of aldehydes/ketones with alkoxides were utilized to react with C_{60} to afford the scarce fullerene acetals and ketals.

Results and Discussion

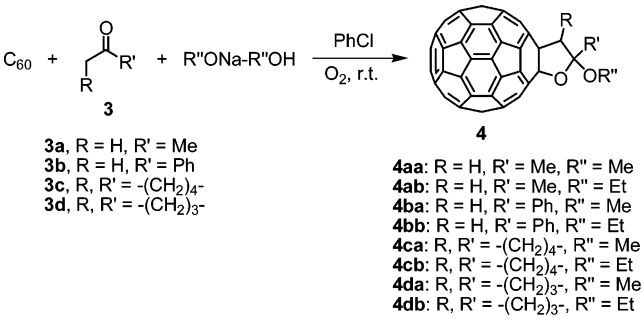
To the best of our knowledge, there has been no report on the reaction of C_{60} with carbanions generated from aldehydes. In an attempt to examine this sort of reaction, three representative aliphatic aldehydes with α-hydrogen, that is, propionaldehyde (**1a**), butyraldehyde (**1b**), and phenylacetaldehyde (**1c**), were chosen. Acetaldehyde was not selected because it is usually sold as an aqueous solution. MeONa−MeOH and EtONa−EtOH, freshly prepared by treating MeOH and EtOH with sodium, were employed as the bases. The reaction of C_{60} with **1a**−**c** and MeONa−MeOH or EtONa−EtOH in anhydrous chlorobenzene under an atmosphere of air at room temperature proceeded well and unexpectedly gave fullerene acetals **2aa**−**cb** (Scheme 1).

Two isomers were formed for all acetals **2aa**−**cb** and could be separated by column chromatography over silica gel except acetal **2cb**. The reaction conditions and yields for the reaction of C_{60} with aldehydes **1a**−**c** and MeONa−MeOH or EtONa−EtOH are listed in Table 1.

It can be seen from Table 1 that the reactions with methoxide were faster than those with ethoxide probably due to higher basicity. Aliphatic aldehydes **1a** and **1b** produced more *cis* isomers. However, the opposite selectivity was observed for phenylacetaldehyde **1c**, which gave more *trans* isomer for both methoxide and ethoxide, and the exact reason is not quite clear now.

The identities of both *cis* and *trans* isomers of acetals **2aa**−**ca** were fully established by MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. All mass spectra of acetals **2aa**−**ca** gave correct molecular ion peaks. In the ^{1}H NMR spectra of *cis* and *trans* isomers of acetals **2aa**−**ca**, the coupling constants between the two vicinal methine protons on the heterocyclic ring were about 4 Hz for the *cis* isomers, while those vanished to zero for the *trans* isomers. This phenomenon is consistent with the previous observations for compounds with similar structural skeletons.[3,8] For acetals **2ab**, **2bb**, and **2cb**, the two methylene protons in the ethoxy group were nonequivalent and split as two double quartets due to the adjacent chiral center. The assignments of *cis* and *trans* isomers were further supported by the NOESY spectra of *cis*-**2aa** and *trans*-**2aa** isomers, which clearly showed a cross-peak between the two vicinal methine protons in the *cis* isomer. In their ^{13}C NMR spectra, the *cis* and *trans* isomers of each product showed similar spectral patterns, and there were at least 48 peaks including some overlapped ones due to the 58 sp^2-carbons of the fullerene moiety, consistent with the C_1 symmetry of the molecular structures. The sp^3-carbons of the C_{60} cage appeared at 70.74−73.12 and 98.40−99.33 ppm. The latter data correspond to the fullerenyl sp^3-carbon connecting to the oxygen atom and agree well with reported data in the literature.[2b,c,3,9] Interestingly, the chemical shifts for the acetal carbons in the *cis* isomers (103.37−106.24 ppm) were shifted upfield about 4−5 ppm relative to those in the *trans* isomers (107.40−111.32 ppm).

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



The substrates could be extended from aldehydes to ketones. Acetone (**3a**), acetophenone (**3b**), cyclohexanone (**3c**), and cyclopentanone (**3d**) were chosen to react with C_{60} and MeONa−MeOH or EtONa−EtOH in anhydrous chlorobenzene at room temperature under aerobic conditions and were found to generate fullerene ketals **4aa**−**db** (Scheme 2).

The reaction conditions and yields for the reaction of C_{60} with ketones **3a**−**d** and MeONa−MeOH or EtONa−EtOH are listed in Table 2.

Unlike the reaction of C_{60} with aldehydes **1a**−**c** and alkoxides that give two acetal isomers, the reaction of C_{60} with ketones **3a**−**d** and alkoxides afforded only one ketal product except for the reaction of C_{60} with **3b**, which produced the additional methanofullerene **5**[5d,10] (Figure 1) as a byproduct.

Ketals **4aa**−**db** were also fully characterized by MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In the ^{1}H NMR spectra of ketals **4aa**−**db**, the two methylene protons on the tetrahydrofuran ring in ketals **4aa**−**bb** appeared as two AB doublets, while the two methylene protons of the ethoxy group in ketals **4ab**, **4bb**, **4cb**, and **4db** were split as two double quartets. In the ^{13}C NMR spectra of ketals **4aa**−**db**, their spectral patterns in the sp^2-carbon region resembled those of acetals **2aa**−**ca**, and two fullerenyl sp^3-carbons and ketal carbon

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TABLE 1. Reactant Molar Ratios, Reaction Times, and Yields of Acetals 2aa−cb

aldehyde **1**	alkoxide	molar ratio (C_{60}:**1**:alkoxide)	reaction time (min)	Product **2** (yield[a]) *cis* isomer	*trans* isomer
CH_3CH_2CHO (**1a**)	MeONa	1:3:5	20	*cis*-**2aa** (25%)	*trans*-**2aa** (13%)
CH_3CH_2CHO (**1a**)	EtONa	1:3:5	60	*cis*-**2ab** (34%)	*trans*-**2ab** (15%)
$CH_3(CH_2)_2CHO$ (**1b**)	MeONa	1:3:5	20	*cis*-**2ba** (32%)	*trans*-**2ba** (7%)
$CH_3(CH_2)_2CHO$ (**1b**)	EtONa	1:3:5	120	*cis*-**2bb** (26%)	*trans*-**2bb** (10%)
$PhCH_2CHO$ (**1c**)	MeONa	1:3:10	30	*cis*-**2ca** (12%)	*trans*-**2ca** (18%)
$PhCH_2CHO$ (**1c**)	EtONa	1:3:10	60	*cis*-**2cb** + *trans*-**2cb** (25%)[b]	

[a] Isolated yield. [b] The polarities of the *cis* and *trans* isomers are almost the same, and the two isomers could not be separated from each other on a silica gel column or Cosmosil Buckyprep column; the *cis* isomer/*trans* isomer ratio was 1:1.4 based on the ^{1}H NMR spectrum.

TABLE 2. Reactant Molar Ratios, Reaction Times, and Yields of Ketals 4aa−db

ketone **3**	alkoxide	molar ratio (C_{60}:**3**:alkoxide)	reaction time (min)	product **4** (yield[a])
CH_3COCH_3 (**3a**)	MeONa	1:2:10	60	**4aa** (32%)
CH_3COCH_3 (**3a**)	EtONa	1:2:10	60	**4ab** (42%)
$PhCOCH_3$ (**3b**)	MeONa	1:2:10	60	**4ba** (29%)
$PhCOCH_3$ (**3b**)	EtONa	1:2:10	60	**4bb** (27%)
 (**3c**)	MeONa	1:1:5	30	4ca (38%)
 (**3c**)	EtONa	1:1:5	60	4cb (22%)
 (**3d**)	MeONa	1:1:5	60	4da (17%)
 (**3d**)	EtONa	1:1:5	60	4db (5%)

[a] Isolated yield.

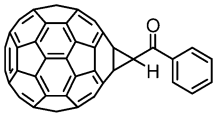
TABLE 3. Relative Energies for *cis* and *trans* Isomers of Products 4ca, 4cb, 4da, and 4db at the B3LYP/3-21G*//AM1 Level

	4ca	**4cb**	**4da**	**4db**
cis isomer (kcal/mol)	4.1	4.5	0.0	0.0
trans isomer (kcal/mol)	0.0	0.0	5.9	5.8

were located at 68.14−73.21, 97.96−100.13, and 107.35−120.81 ppm, respectively, reflecting structural similarity to acetals **2aa**−**ca**.

Even though both *cis* and *trans* isomers could be possibly formed for ketals **4ca**, **4cb**, **4da**, and **4db** (Figure 2), only one isomer was obtained.

The NOESY spectra of ketals **4ca**, **4cb**, **4da**, and **4db** could not give any affirmative cross-peaks between the methine proton and methoxy/ethoxy group probably because the space distance between them exceeded the NOE-observable correlating distance by the employed NMR spectrometer. Hence, theoretical calculations were exploited to obtain the relative stabilities of their *cis* and *trans* isomers. The relative energies of the *cis* and *trans* isomers of ketals **4ca**, **4cb**, **4da**, and **4db** calculated at the B3LYP/3-21G*//AM1 level[12] (Table 3) showed the *trans* isomers of ketals **4ca** and **4cb** were at least 4 kcal/mol more stable than their *cis* isomers, while the *cis* isomers of ketals **4da** and **4db** were about 6 kcal/mol more stable than their *trans* isomers. Therefore, the obtained isomers for ketals **4ca** and **4cb** were probably assigned as the *trans* isomers, and those of ketals **4da** and **4db** as the *cis* isomers. These assignments were also consistent with their chemical shifts of the ketal carbons of products **4ca**, **4cb**, **4da**, and **4db**. The chemical shift of a ketal carbon is usually shifted downfield a few parts per million relative to that of the corresponding acetal carbon. Considering the orientation of the hydrogen and alkoxy groups, the *trans* isomers of ketals **4ca**, **4cb**, **4da**, and **4db** should correspond to the *cis* isomers of acetals **2aa**−**2cb**. Further, taking into account of the chemical shifts for the acetal carbons in the *cis* isomers (103.37−106.24 ppm) and in the *trans* isomers (107.40−111.32 ppm) of acetals **2aa**−**2ca**, the observation of the chemical shifts for the ketal carbons of products **4ca** and **4cb** at 109.25 and 108.88 ppm supports their assignments as the *trans* isomers. Similar arguments also validate the assignments of ketals **4da** and **4db** as the *cis* isomers.



5

FIGURE 1. Structure of methanofullerene **5**.

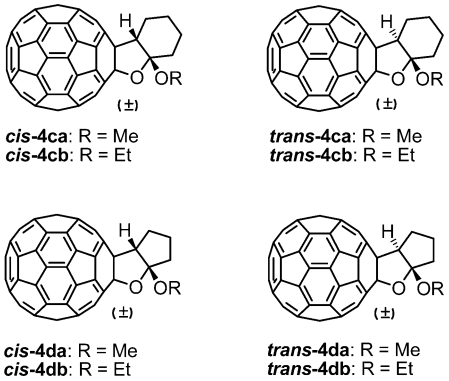
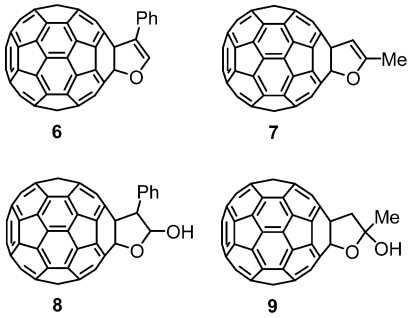


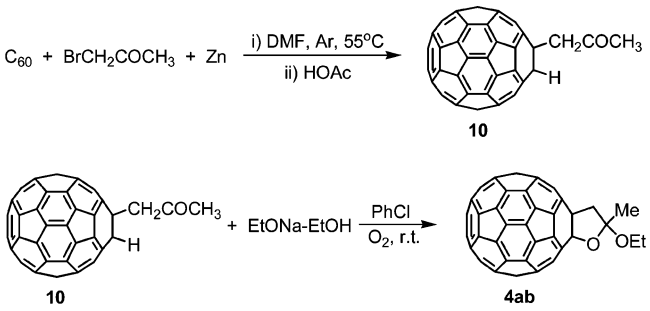
FIGURE 2. Structures of the *cis* and *trans* isomers of ketals **4ca**, **4cb**, **4da**, and **4db**.



6 **7** **8** **9**

FIGURE 3. Structures of compounds **6**−**9**.

SCHEME 3. Reaction of C_{60} with Bromoacetone and Zinc, and Then with Ethoxide

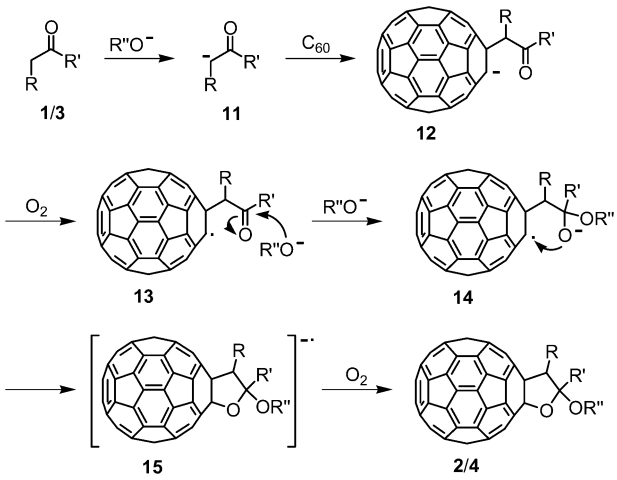


It was found that oxygen was necessary for the formation of acetals **2aa**−**cb** and ketals **4aa**−**db**. When oxygen was strictly excluded from the reaction mixtures, no acetals **2aa**−**cb** and ketals **4aa**−**db** could be obtained. Control experiments showed that bubbling of pure oxygen into the reaction mixtures accelerated the reaction processes as shorter reaction times were required to reach the same product yields. β-Keto esters,[5d,6a] β-diketones,[5d,6a] and methyl ketones[5d] could react with C_{60} in the presence of a base and gave C_{60}-fused dihydrofuran derivatives or methanofullerenes. It was suggested that carbanions formed by deprotonation from the substrates first attacked C_{60} to generate fullerene anions, and subsequent oxidation and intramolecular cyclization afforded the fullerene products. Therefore, it is reasonable to speculate that fullerene acetals and ketals were formed through the C_{60}-fused dihydrofuran intermediates, which then reacted with MeONa−MeOH/EtONa−EtOH to generate the final products. However, C_{60}-fused dihydrofuran derivatives **6**[3] and **7**[3] (Figure 2) could not react with MeONa−MeOH/EtONa−EtOH to give acetals **2ca**/**2cb** and ketals **4aa**/**4ab** under an atmosphere of air at room temperature. Furthermore, hemiacetal **8**[3] and hemiketal **9**[3] (Figure 2), potential precursors of compounds **6** and **7**, also failed to react with MeONa−MeOH/EtONa−EtOH to obtain acetals **2ca**/**2cb** and ketals **4aa**/**4ab** under the same conditions.

In order to gain more insight into the reaction mechanism, we synthesized compound **10** in 6% yield by the reaction of C_{60} with bromoacetone and zinc (1:25:50) in DMF, followed by quenching with acetic acid (Scheme 3).[11] The proton attached to the fullerene skeleton is quite acidic and can be easily deprotonated by a base to obtain the corresponding fullerene anion. We found that treatment of compound **10** with EtONa−EtOH (1:5) could produce ketal **4ab** in 38% yield (Scheme 3).

On the basis of the above results, the proposed reaction mechanism for the formation of fullerene acetals **2** and ketals **4** is outlined in Scheme 4.

SCHEME 4. Proposed Reaction Mechanism for the Formation of Fullerene Acetals and Ketals



The carbanion **11** generated by deprotonation at the α-carbon of an aldehyde or a ketone attacks C_{60} to give fullerene anion **12**. Oxidation of anion **12** by oxygen produces radical **13**. Addition of the alkoxide to the carbonyl group on the side chain of species **13** leads to the anionic form of an acyclic hemiacetal/hemiketal **14**. Ring closure of the intermediate **14** by an intramolecular nucleophilic addition to the fullerene skeleton affords radical anion **15**, which is oxidized by air to give acetal **2** or ketal **4**.

Conclusion

Combinations of aldehydes/ketones with alkoxides were employed to react with C_{60} to afford the scarce fullerene acetals and ketals. The reaction of C_{60} with propionaldehyde (**1a**) (butyraldehyde (**1b**) or phenylacetaldehyde (**1c**)) and MeONa−MeOH or EtONa−EtOH in anhydrous chlorobenzene under aerobic conditions at room temperature unexpectedly gave fullerene acetals **2aa**−**cb**, which existed as both *cis* and *trans* isomers. On the other hand, the reaction of C_{60} with acetone (**3a**) (acetophenone (**3b**), cyclohexanone (**3c**), or cyclopentanone (**3d**)) and MeONa−MeOH or EtONa−EtOH under the same conditions afforded fullerene ketals **4aa**−**db** as single products. Among them, ketals **4ca** and **4cb** were assigned as the *trans* isomers, while ketals **4da** and **4db** were assigned the *cis* isomers. On the basis of further experimental results, a reaction mechanism is proposed to explain the formation of acetals **2aa**−**cb** and ketals **4aa**−**db**.

Experimental Section

Preparation of Fullerene Acetal 2aa. A mixture of C_{60} (36.0 mg, 0.05 mmol) and propionaldehyde (**1a**) (11 μL, 0.15 mmol) was dissolved in anhydrous chlorobenzene (15 mL), and then MeONa−MeOH (146 μL, 0.25 mmol, freshly prepared by treating 5 mL of MeOH with 198 mg of sodium) was added. The reaction mixture was stirred under an atmosphere of air and at room temperature for 20 min (monitored by TLC) and was filtered through a silica gel plug in order 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} (9.6 mg, 27%), *cis*-**2aa** (10.3 mg, 25%), and then *trans*-**2aa** (5.3 mg, 13%).

***cis*-2aa:** ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 5.84 (d, J = 4.0 Hz, 1H), 4.05 (qd, J = 7.1, 4.0 Hz, 1H), 3.84 (s, 3H), 1.86 (d, J =

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7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation agent) (all 1C unless indicated) δ 155.99, 152.59, 151.54, 148.55, 147.79, 147.14, 146.29, 146.15 (2C), 146.10, 146.02, 146.01, 145.84, 145.83, 145.79, 145.70, 145.67, 145.66, 145.34 (2C), 145.12, 145.09, 145.06, 144.98 (2C), 144.93, 144.90, 144.83, 144.62, 144.47, 144.46, 144.10, 142.75, 142.70, 142.49 (2C), 142.43 (2C), 142.39, 142.13, 142.09, 142.04, 142.01 (3C), 141.85, 141.79, 141.64, 141.49, 141.32, 139.94, 139.54, 139.44, 139.30, 137.80, 137.60, 137.33, 134.98, 106.24, 99.04 (sp^3-*C* of C_{60}), 71.07 (sp^3-*C* of C_{60}), 55.32, 53.10, 12.70; FT-IR ν/cm^{-1} (KBr) 2948, 2921, 2827, 1511, 1428, 1378, 1353, 1304, 1179, 1164, 1136, 1102, 1075, 1009, 967, 934, 904, 765, 592, 576, 564, 553, 526, 494; UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 254 (5.23), 312 (4.68), 427 (3.56), 455 (3.40), 694 (2.86); MS (ESI) *m*/*z* 808 (M^-).

***trans*-2aa:** ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 5.69 (s, 1H), 4.10 (q, J = 7.4 Hz, 1H), 3.83 (s, 3H), 1.95 (d, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation agent) (all 1C unless indicated) δ 155.78, 153.28, 150.90, 149.15, 147.87, 147.27, 146.29, 146.27, 146.16 (2C), 145.96, 145.94, 145.89, 145.87, 145.75, 145.72, 145.69, 145.48, 145.43, 145.24, 145.16, 145.11, 145.08 (2C), 145.07, 145.01 (2C), 144.91, 144.59 (2C), 144.53, 144.24, 142.84, 142.78, 142.59, 142.53, 142.49, 142.45, 142.38, 142.17, 142.13, 142.11, 142.04, 142.01 (2C), 141.85, 141.78, 141.75, 141.62, 141.29, 139.80, 139.68, 139.53, 139.41, 138.34, 137.57, 136.90, 136.54, 111.32, 98.66 (sp^3-*C* of C_{60}), 71.24 (sp^3-*C* of C_{60}), 55.59, 52.45, 18.95; FT-IR ν/cm^{-1} (KBr) 2950, 2922, 2827, 1450, 1428, 1379, 1359, 1183, 1112, 1099, 1060, 1006, 967, 957, 940, 905, 766, 596, 575, 563, 553, 526, 511, 481; UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 253 (5.18), 313 (4.59), 428 (3.45), 453 (3.25), 694 (2.57); MS (ESI) *m*/*z* 808 (M^-).

Preparation of Fullerene Ketal 4aa. By the same procedure as for the preparation of acetal **2aa**, the reaction of C_{60} (36.0 mg, 0.05 mmol) with acetone (**3a**) (7 μL, 0.10 mmol) and MeONa−MeOH (0.50 mmol) for 60 min afforded unreacted C_{60} (17.0 mg, 47%) and **4aa** (12.9 mg, 32%).

4aa: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 3.99 (d, J = 12.5 Hz, 1H), 3.79 (d, J = 12.5 Hz, 1H), 3.74 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation agent) (all 1C unless indicated) δ 156.00, 155.40, 150.58, 148.79, 147.75, 147.11, 146.10, 146.09, 146.03, 145.98, 145.87, 145.78, 145.76 (2C), 145.64 (2C), 145.36 (2C), 145.09 (2C), 145.05, 144.99 (2C), 144.92 (2C), 144.87, 144.84 (2C), 144.50, 144.47, 144.40, 144.08, 142.68, 142.65, 142.40 (2C), 142.33 (2C), 142.25 (2C), 142.02, 141.94, 141.89 (3C), 141.71, 141.67, 141.61, 141.35, 141.27, 139.76, 139.67, 139.33, 139.16, 137.77, 137.54, 137.00, 134.97, 107.61, 99.02 (sp^3-*C* of C_{60}), 68.29 (sp^3-*C* of C_{60}), 53.38, 49.94, 20.35; FT-IR ν/cm^{-1} (KBr) 2983, 2927, 2825, 1511, 1462, 1431, 1377, 1243, 1218, 1184, 1172, 1113, 1076, 1068, 1044, 996, 934, 871, 768, 595, 575, 553, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 256 (5.15), 313 (4.68), 428 (3.45), 453 (3.22), 692 (2.20); MS (ESI) *m*/*z* 808 (M^-).

Preparation of Compound 10. By following the reported procedure,[11] the reaction of C_{60} (144 mg, 0.2 mmol) with bromoacetone (420 μL, 5.0 mmol) and Zn dust (0.65 g, 10.0 mmol) in DMF for 40 min gave unreacted C_{60} (15.3 mg, 11%) and compound **10** (9.0 mg, 6%).

Compound 10: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 6.59 (s, 1H), 4.60 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 203.55 (1C), 153.87, 153.16, 147.13 (1C), 146.86 (1C), 146.66, 146.01, 145.95, 145.79 (4C), 145.50, 145.25, 145.17, 145.02 (4C), 144.96, 144.48, 144.12, 142.87, 142.22, 142.14, 141.73, 141.70, 141.51, 141.33, 141.23 (4C), 139.86, 139.80, 136.64, 136.22, 60.59, 59.02, 57.08, 30.60; FT-IR ν/cm^{-1} (KBr) 2964, 2907, 1722, 1530, 1511, 1460, 1424, 1393, 1337, 1261, 1230, 1164, 1097, 1025, 805, 614, 575, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 256 (4.99), 318 (4.47), 433 (3.53), 706 (2.57); MS (APCI) *m*/*z* 777 (M − 1).

Preparation of Ketal 4ab from Compound 10. To the chlorobenzene solution (15 mL) of EtONa−EtOH (5 equiv) was added compound **10** (10.1 mg) dissolved in dichlorobenzene (5 mL) dropwise over 20 min in the presence of air. Stirring was continued for another 20 min. The reaction mixture was filtered through a silica gel plug in order 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 ketal **4ab** (4.1 mg, 38%).

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Supporting Information Available: Experimental procedures and spectral data for acetals **2ab**−**cb** and ketals **4ab**−**db**, NMR spectra of acetals **2aa**−**cb**, ketals **4aa**−**db**, and compound **10**, AM1 optimized geometries, Cartesian coordinates, and B3LYP/3-21G*// AM1 total energies of *cis* and *trans* isomers of ketals **4ca**, **4cb**, **4da**, and **4db**. This material is available free of charge via the Internet at http://pubs.acs.org.

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