JOC The Journal of Organic Chemistry

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DMAP-Catalyzed [3 + 2] and [4 + 2] Cycloaddition Reactions between [60]Fullerene and Unmodified Morita–Baylis–Hillman Adducts in the Presence of Ac_2O

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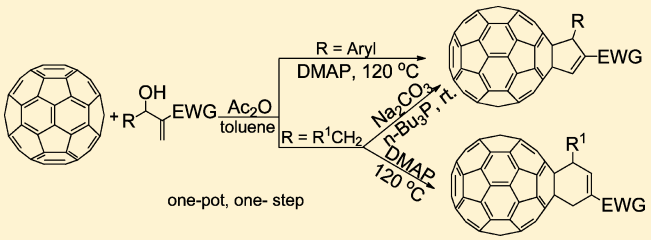
Supporting Information

ABSTRACT: One-step DMAP-catalyzed [3 + 2] and [4 + 2] cycloaddition reactions between C_{60} and unmodified Morita–Baylis–Hillman adducts in the presence of Ac_2O have been developed for the easy preparation of cyclopentene- and cyclohexene-fused [60]fullerene derivatives. When the MBH adducts bear an alkyl group, two different reaction pathways could be controlled selectively depending on the conditions.



INTRODUCTION

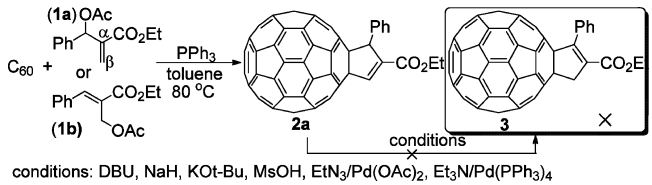
The functionalization of [60]fullerene with various organic functional groups is an important subject in fullerene chemistry for further material and medicinal applications. A remarkable array of their chemical reactions has been explored over the last two decades.[1] Among which, 1,3-dipolar cycloaddition is one of the most used methodology to construct five-membered ring-fused [60]fullerene derivatives containing one or two heteroatoms. Only a limited number of methods for the preparation of [60]fullerene fused cyclopentane and cyclopentene derivatives have been reported up to now, such as the [3 + 2] reaction of cyclopropanone or cyclopropenone ketal with C_{60},[2] reaction of C_{60} anion with 1,3-dihalogenated compounds or cyano-substituted alkenes,[3] cycloaddition reaction of C_{60} with different zwitterionic species derived from dimethyl acetylenedicarboxylate,[4] phosphine-catalyzed cycloaddition of C_{60} with 2,3-dienoates or electron-deficient alkynes,[5] and photoreaction of C_{60} with alkene linked with a cyclopropyl moiety through a biradical intermediate.[6] Thermal reactions of [60]fullerene with tertiary amines and aldehydes to give cyclopentafullerene derivatives were reported by the Wang group.[7a] Recently, they also reported the synthesis of C_{60}-Indane derivatives through the addition of $AlCl_3$ to the Mn (III)-mediated reaction of C_{60} with α-aryl active methelene compounds or mesitylenesulfonic acid mediated rearrangement of C_{60}-fused tetrahydroisoquinolines.[7b,c]

The Morita–Baylis–Hillman (MBH) reaction is one of the most atom-economic reactions for the construction of densely functionalized products, which are useful intermediates in organic synthesis as C_3 synthons.[8] In the past few years, Lu and co-workers pioneered the use of the modified MBH adducts (-X, -OAc, -OBoc) in [3 + 2] cyclizations and various cycloadditions.[9] Afterward, this new kind of [3 + 2] annulation reaction was investigated on different C=C,[10] C=N,[11] and N=N[12] double bonds. The Lu, Barbas, Liu, and Shi groups have successfully applied this strategy to synthesize enantiopure spirocyclopenteneoxindole derivatives or functionalized bicyclic imides[13] and the Tang group has investigated the intramolecular [3 + 2] reaction.[14] To the best of our knowledge, the hydroxyl group on MBH adducts must be transformed to OAc, OBoc, or X (X = Cl, Br) and a phosphine must be used as the catalyst in this strategy and this kind of annulation has not been applied to the functionalization of C_{60} yet. In the context of our general interest in fullerene chemistry,[15] herein, we reported the DMAP-catalyzed [3 + 2] and [4 + 2] cyclization reactions between [60]fullerene and unmodified MBH adducts in the presence of Ac_2O to afford cyclopentene- and cyclohexene-fused [60]-fullerene derivatives, respectively.

RESULTS AND DISCUSSION

We initiated our studies by evaluating the reaction of C_{60} (36.0 mg, 0.05 mmol) with ethyl 2-(acetoxy(phenyl)methyl)acrylate **1a** (2 equiv) using 20 mol % PPh_3 as the catalyst in toluene at 120 °C (Scheme 1). To our delight, the desired [3 + 2] cycloaddition product **2a** was obtained as the single product in 29% yield after

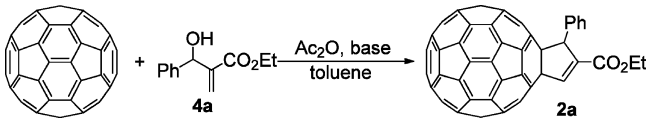
Scheme 1. Phosphine-Catalyzed [3 + 2] Annulations of C_{60} with Acetyl-Modified MBH Adduct 1



Received: December 4, 2012
Published: January 4, 2013

   dx.doi.org/10.1021/jo3025797 | J. Org. Chem. 2013, 78, 1163–1170

Table 1. Screening of the One-Step Reaction Conditions[a]



entry	C_{60}/**4a**/Ac_2O/base/PPh_3	base	T (°C)	time (h)	yield (%)[b]
1	1:5:5:5:1	DMAP	80	24	39 (82)
2	1:5:5:5:1	DMAP	120	1.5	37 (80)
3	1:5:5:5:0	DMAP	120	2	36 (86)
4	1:5:5:5:0	K_2CO_3	120	10	0
5	1:5:5:5:0	Et_3N	120	10	0
6	1:5:5:5:0	*N*-methyl imidazole	120	10	trace
7	1:5:5:5:0	pyridine	120	10	trace
8	1:5:5:5:0	DBU	120	10	0
9	**1:3:3:3:0**	**DMAP**	**120**	**4**	**36 (83)**
10	1:2:2:2:0	DMAP	120	6	30 (89)
11	1:1:1:1:0	DMAP	120	10	19 (90)

[a]To a mixture of C_{60} (36 mg, 0.05 mmol), **4a**, base, and PPh_3 in 16 mL of dry toluene was added Ac_2O. The mixture was then stirred at the indicated temperature in a preheated oil bath. [b]Isolated yield. Values in parentheses were based on consumed C_{60}.

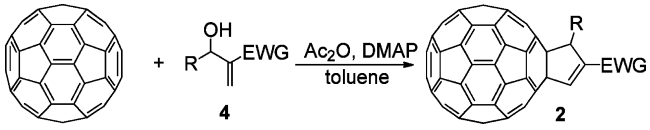
24 h. As commonly proposed in the literature, an allylic *P*-ylide formed through attacking of phosphine on the *β*-C of **1a**. We conjectured that, if ethyl 2-(acetoxymethyl)-3-phenylacrylate **1b** was used as the substrate, the isomer **3** would be generated. Nevertheless, the same product **2a** was isolated in 27% yield after 24 h under the similar conditions. The compound **3**, as the isomer of **2a**, was assumed to be more stable than **2a** for the existence of a conjugation effect between the phenyl group and double bonds. However, under different conditions, such as DBU, NaH, *t*-BuOK, MsOH, Et_3N/$Pd(OAc)_2$, or Et_3N/$Pd(PPh_3)_4$, **2a** could not be converted to **3** either at room temperature or at 120 °C. We think that the big steric hindrance between the phenyl group and the fullerene skeleton increases the instablility of **3**.

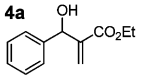
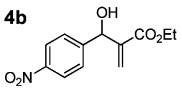
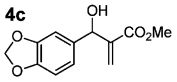
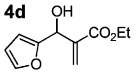
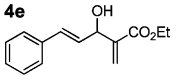
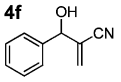
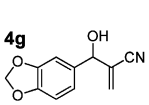
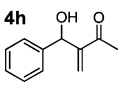
In an attempt to make this approach more efficient, a one-step [3 + 2] cycloaddition directly from unmodified MBH adduct **4a** and C_{60} was tried. Ac_2O and a base were used as additive reagents to generate **1a** in situ. The influence of base, molar ratio of reagents, and temperature on the reaction was investigated in detail (Table 1).

Under the molar ratio of C_{60}/**4a**/Ac_2O/DMAP/PPh_3 as 1:5:5:5:1, **2a** was obtained as expected in 39% yield after stirring at 80 °C for 24 h (Table 1, entry 1). When the reaction temperature was increased to 120 °C, a similar yield was obtained in a shorter reaction time (1.5 h) (Table 1, entry 2). Moreover, to our surprise, in the absence of PPh_3, **2a** also could be formed in 36% yield (Table 1, entry 3). It was the first example that the amine, but not the phosphine, catalyzed this kind of intermolecular [3 + 2] reaction. The examination of different bases, such as K_2CO_3, Et_3N, *N*-methyl imidazole, pyridine, and DBU, revealed that only DMAP was the effective base in the absence of phosphine (Table 1, entries 4−8), and DBU gave an unidentified precipitate with the full conversion of C_{60}. Reducing the employed amount of **4a**, Ac_2O, and DMAP to 3 equiv also gave **2a** in 36% yield in a slightly longer time (Table 1, entry 9). Further reducing the amount of starting materials led to a longer reaction time and a lower yield of **2a** (Table 1, entries 10 and 11). Eventually, the molar ratio of C_{60}/**4a**/Ac_2O/DMAP as 1:3:3:3 and the reaction temperature as 120 °C were selected as the optimal conditions for the [3 + 2] cycloaddition reaction.

To determine the generality of this methodology, a variety of MBH adducts **4**, derived from aromatic aldehydes, were used to react with C_{60} (Table 2). All of the reactions were completed in 3−10 h with a moderate to good yield of **2**. The electronic

Table 2. Substrate Scope for the [3 + 2] Annulations[a,b]



entry	substrate	product	yield (%)[b]
1	**4a** 	**2a**	36 (83)
2	**4b** 	**2b**	29 (79)
3	**4c** 	**2c**	33 (90)
4	**4d** 	**2d**	31 (76)
5	**4e** 	**2e**	19 (74)
6	**4f** 	**2f**	35 (90)
7	**4g** 	**2g**	33 (86)
8	**4h** 	**2h**	29 (79)

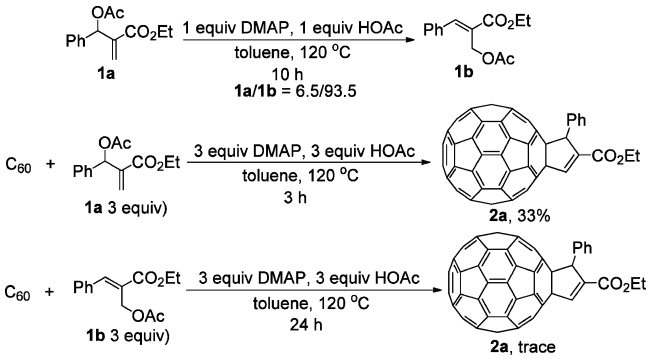
[a]All the reactions were performed with 0.05 mmol of C_{60} in the molar ratio of C_{60}/**4**/Ac_2O/DMAP = 1:3:3:3 in 16 mL of dry toluene at 120 °C for 3−10 h. [b]Isolated yield. Values in parentheses were based on consumed C_{60}.

dx.doi.org/10.1021/jo3025797 | J. Org. Chem. 2013, 78, 1163−1170

properties of the substituent on the aromatic ring had little or no influence on the reactions. A substrate with a heteroaromatic group also reacted, affording the corresponding derivative **2d** with 31% yield (Table 2, entry 4). All in all, different functional groups such as ester, nitrile, and ketone, could be introduced to the fullerene skeleton using this method.

Under the DMAP-catalyzed [3 + 2] reaction conditions, isomerization of the acetyl-modified MBH product **1a** into **1b** was observed. When **1a** was treated with 1 equiv of DMAP and 1 equiv of HOAc in toluene at 120 °C for 10 h, the ratio of **1a**/**1b** changed from 100/0 to 6.5/93.5, as determined by the ^{1}H NMR analysis (Scheme 2). To determine which one is the active species, C_{60} was reacted with 3 equiv of **1a** and 3 equiv of **1b**, respectively, in the presence of 3 equiv of DMAP and 3 equiv of HOAc (the in situ generated **1a** in a one-step reaction from unmodified MBH prouduct, Ac_2O, and DMAP would produce the same amount of HOAc). **1a** gave the desired product **2a** in 33% yield after 3 h. However, **1b** only gave a trace of **2a** after 24 h. When a catalytic amount of Ph_3P was added to the mixture and it was stirred for another 2 h, the reaction worked again. This proved that phosphine was more active than DMAP in this kind of [3 + 2] reaction and **1a** is the actual active species in the absence of phosphine.

Scheme 2. Active Species in the DMAP-Catalyzed [3 + 2] Reaction



The [3 + 2] cycloaddition reaction tolerated different aromatic moieties in the MBH adducts **4** (R = Ar). When the MBH adduct **5a** bearing an alkyl group was employed in the reaction, no [3 + 2] product **7a** was observed. Instead, the [4 + 2] cycloaddition product **6a** was isolated as the single product (Table 3, entry 1). Recently, there was a report on the amine-catalyzed [4 + 2] annulation of MBH allylic acetates with electron-deficient alkenes.[16] Presumably, the high reaction temperature was beneficial to the elimination of HOAc and generation of the diene intermediate. Reducing the temperature to rt resulted in nearly no reaction (Table 3, entry 2). Various conditions were tried to get the [3 + 2] product **7a**. With an additive of 0.1 equiv of PPh_3, no **7a** was observed yet (Table 3, entry 3). We wanted to reduce the reaction temperature and used more active *n*-Bu_3P instead of PPh_3. When 0.1 equiv of *n*-Bu_3P was used, the reaction proceeded slowly and only a trace of **6a** was observed on TLC analysis after 14 h (Table 3, entry 4). When the amount of *n*-Bu_3P was increased to 0.5 equiv, the desired [3 + 2] product **7a** was obtained in 10% yield accompanying with 6% of [4 + 2] product **6a** (Table 3, entry 5). A further increase in the amount of *n*-Bu_3P to 1 equiv resulted in the improvement on the selectivity of the [3 + 2] product **7a** in 24% yield accompanying with 6% of [4 + 2] product **6a** (Table 3, entry 6). A trend toward an increased ratio of **7a**/**6a** as the increased amount of *n*-Bu_3P was observed. When Na_2CO_3 was used as the base, higher selectivity and yield of **7a** could be obtained (Table 3, entry 7). When **5b**−**5d** was employed in the reaction, the [3 + 2] products **7b**−**7d** and [4 + 2] products **6b**−**6d** also could be selectively formed under Na_2CO_3/*n*-Bu_3P and DMAP conditions, respectively (Scheme 3).

Scheme 3. [3 + 2] and [4 + 2] Cycloaddition between C_{60} and Unmodified MBH Adducts Bearing an Alkyl Group

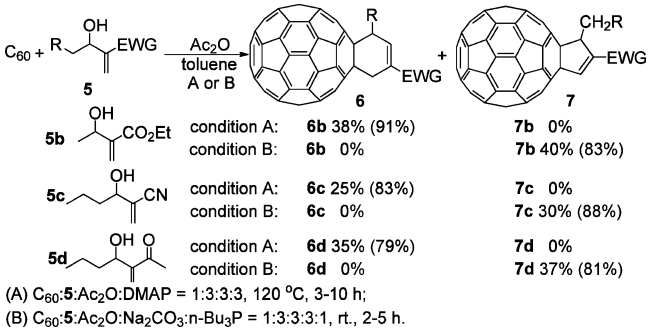
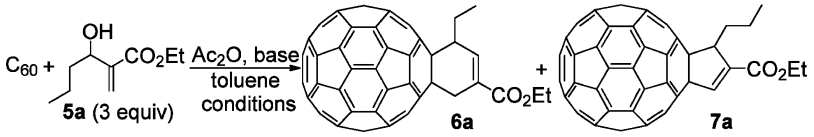


Table 3. Reaction between C_{60} and 5a Bearing an Alkyl Group in the Presence of Ac_2O and DMAP[a]



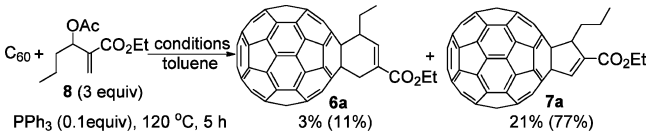
entry	conditions	**6a** (%)[b]	**7a** (%)[b]
1	**DMAP, 120 °C, 3 h**	**35 (87)**	**0**
2	DMAP, rt, 14 h	trace	0
3	DMAP, PPh_3 (0.1 equiv), 120 °C, 3 h	34 (90)	0
4	DMAP, *n*-Bu_3P (0.1 equiv), rt, 14 h	trace	0
5	DMAP, *n*-Bu_3P (0.5 equiv), rt, 14 h	6 (33)	10 (55)
6	DMAP, *n*-Bu_3P (1 equiv), rt, 9 h	6 (17)	24 (68)
7	**Na_2CO_3, *n*-Bu_3P (1 equiv), rt, 9 h**	**5 (10)**	**36 (72)**
8	Na_2CO_3, PPh_3 (0.1 equiv), 120 °C, 9 h	trace	6 (92)

[a]All the reactions were performed with 0.05 mmol of C_{60} in the molar ratio of C_{60}/**5**/Ac_2O/base = 1:3:3:3 and the indicated amount of phosphine in 16 mL of dry toluene. [b]Isolated yield. Values in parentheses were based on consumed C_{60}.

dx.doi.org/10.1021/jo3025797 | J. Org. Chem. 2013, 78, 1163−1170

It was clear that DMAP could catalyze both [3 + 2] and [4 + 2] reactions and phosphine is beneficial to the [3 + 2] reaction. With the MBH adducts derived from aliphatic aldehyde with an α-H, the [4 + 2] reaction proceeded much faster than the [3 + 2] reaction under DMAP conditions. To establish whether the phosphine could also catalyze the [4 + 2] reaction, the acetyl-modified BH adduct **8** was prepared and treated with PPh_3 and *n*-Bu_3P, respectively (Scheme 4). When PPh_3 was selected as the

Scheme 4. Reaction of C_{60} with Acetyl-Modified MBH Adduct 8



	6a	7a
PPh_3 (0.1equiv), 120 °C, 5 h	3% (11%)	21% (77%)
PPh_3 (0.1equiv), rt, 20 h	0	0
n-Bu_3P (0.1equiv), 120 °C, 20 min	41% (76%)[a]	6% (11%)[a]
n-Bu_3P (0.1equiv), rt., 2.5 h	21% (44%)	19% (40%)
n-Bu_3P (0.5equiv), rt., 1.5 h	15% (29%)	28% (54%)
n-Bu_3P (1equiv), rt., 40 min	6% (10%)	38% (64%)

[a] 1 equiv of substrate 8 was used.

catalyst, the [3 + 2] product **7a** was isolated as the main product under thermal conditions (**7a**/**6a** = 7:1). However, no reaction occurred at room temperature. When *n*-Bu_3P was used, an interesting phenomenon was observed. At 120 °C, the [4 + 2] reaction was predominant using a catalytic amount of *n*-Bu_3P. When the temperature was increased to rt, a trend of an increased ratio of **7a**/**6a** from 19/21 to 38/6 was observed as the amount of *n*-Bu_3P was increased from 0.1 to 1 equiv. It revealed that the phosphine catalyzed not only the [3 + 2] reaction but also the [4 + 2] reaction because it also could act as an organic base like DMAP. We think that the basicity of *n*-Bu_3P was higher than that of PPh_3, which thus gave more [4 + 2] product when the same amount of phosphine was used. The origin of the trend of increased ratio of **7a**/**6a** as the amount of *n*-Bu_3P was increased is not clear now.

The structures of C_{60}-fused cyclopentene and cyclohexene derivatives **2a**−**2h**, **7a**−**7d**, **6a**, and **6d** were fully established by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectral data.[17] Taking **2a** as an example, the MALDI-FTMS spectra of **2a** displayed the [M^+] peak at 908.0816. The ^{1}H NMR spectrum of **2a** showed two doublets at 8.08 and 6.21 ppm with a coupling constant of 1.8 Hz for the vinyl and methine hydrogen, two dq peaks at 4.29 and 4.36 ppm and a triplet at 1.28 ppm for the ethyl proton. It should be noted that all phenyl protons are magnetically inequivalent, probably due to the restricted rotation of the phenyl ring.[3b] In the case of compound **2e**, this phenomenon was not observed due to the long distance between the phenyl ring and the C_{60} skeleton. In the ^{13}C NMR spectra of **2a**, there are 59 partially overlapped peaks in the region of 127−157 ppm for all the sp^2 carbons, one peak at 164.2 ppm for the carbonyl group, two peaks at 14.29 and 61.34 ppm for the ethyl group, one peak at 63.35 ppm for the methine carbon, and two peaks at 74.86 and 77.26 ppm for the two sp^3 carbons of the C_{60}, consistent with the cyclopentene structure. The UV−vis spectrum of **2a** exhibited a characteristic absorption for the 1,2-adducts of C_{60} at 431 nm.

The structures of **6** and **7** could be easily discriminated through their ^{1}H NMR spectra (Figure 1). For the example of **6a** versus **7a**, the H_a and H_b in **6a** directly attached with the fullerene had a noticeable downfield shift and the splitting pattern was different from that of the CH_2 group in **7a**. In the ^{1}H NMR

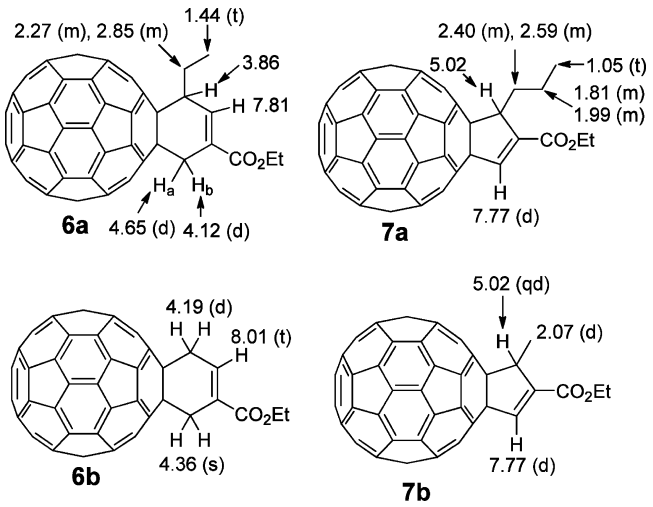


Figure 1. Difference between **6** and **7** in their ^{1}H NMR spectra.

spectrum of **6b**, the two CH_2 groups showed a singlet at 4.36 ppm and a doublet at 4.19 ppm, respectively. However, no CH_2 group existed in the structure of **7b**. The methyl group showed a doublet at 2.07 ppm, and the methine group showed a qd peak at 5.02 ppm. Furthermore, there were about 30 peaks for the fullerene skeleton in **6b** due to the C_s symmetry. The molecular structure of **7b** had no symmetry and showed about 60 peaks for the fullerene skeleton.

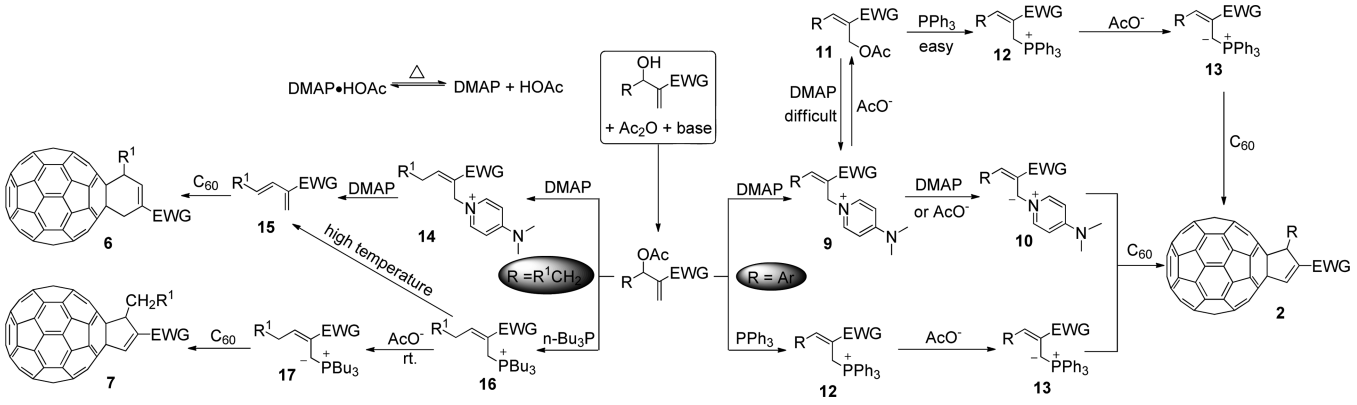
A plausible mechanism is proposed in Scheme 5. The acetyl-modified MBH product is generated in situ from the MBH product, Ac_2O, and base. When R is an aromatic group, a pyridinium salt **9** is formed through an S_N process under DMAP conditions. *N*-ylide intermediate **10** or the isomer **11** could be, respectively, formed through S_N reaction or deprotonation in the presence of AcO^-. **10** serves as a surrogate of the 1,3-dipole to undergo a [3 + 2] cycloaddition with C_{60} to generate **2**. **11** is difficult to regenerate **9** under the action of DMAP. However, in the presence of phosphine, it can generate the *P*-ylide, which reacts with C_{60} to generate **2**. When R is an aliphatic group, pyridinium salt **14** and phosphonium salt **16** were generated, respectively, under DMAP or *n*-Bu_3P/Na_2CO_3 conditions. A competing deprotonation of the γ-H and then elimination of DMAP from **14** provide the highly reactive 1,3-diene intermediate **15**, and subsequent Diels−Alder reaction with C_{60} affords the [4 + 2] products **6**. As for the phosphonium salt **16**, two competing reactions exist depending on the reaction temperature. At room temperature, a *P*-ylide **17** is preferentially formed through an S_N-deprotonation process, which undergoes a [3 + 2] reaction with C_{60} to give the product **7**. More 1,3-diene intermediate **15** yields along with the increase of temperature, which leads to the generation of competing product **6**.

CONCLUSION

In conclusion, one-step DMAP-catalyzed [3 + 2] and [4 + 2] cycloaddition reactions of C_{60} with unmodified MBH products in the presence of Ac_2O were realized and led to the easy preparation of cyclopentene- and cyclohexene-fused [60]-fullerene derivatives, respectively. The MBH adducts bearing aromatic groups only undertake the [3 + 2] process. It was the first example that DMAP catalyzed this kind of [3 + 2] reaction through the *N*-ylide, but not the *P*-ylide. The MBH adducts bearing alkyl groups could give the [3 + 2] and [4 + 2] products selectively depending on the reaction conditions. Moreover, the

dx.doi.org/10.1021/jo3025797 | J. Org. Chem. 2013, 78, 1163−1170

Scheme 5. Plausible Mechanism



difference between PPh_3 and n-Bu_3P on the [3 + 2] reaction was also investigated. A possible reaction mechanism was proposed to explain the formation of C_{60}-fused cyclopentene/cyclohexene derivatives.

EXPERIMENTAL SECTION

Preparation of 1a and 1b. To a mixture of **4a** (228 mg, 1.1 mmol) and pyridine (119 mg, 1.5 mmol) in 8 mL of dry dichloromethane was added dropwise a solution of acetyl chloride (117 mg, 1.5 mmol) in 5 mL of dichloromethane at 0 °C. The temperature was kept for 5−10 min, and then warmed to room temperature, and the mixture continued to stir for 4−5 h. After completion of the reaction, detected by TLC, 20 mL of water was added to the mixture and then extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent, followed by column chromatography on silica gel using petroleum ether/EtOAc (10:1) as the eluent, gave the corresponding product **1a** (219 mg, 80%) as a colorless oil. **1a**:[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.40 (m, 5H), 6.68 (s, 1H), 6.40 (t, J = 0.9 Hz, 1H), 5.84 (dd, J = 1.3, 1.0 Hz, 1H), 4.17 (dq, J = 10.8, 7.2 Hz, 1H), 4.13 (dq, J = 10.8, 7.2 Hz, 1H), 2.11 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H).

To a 25 mL one-neck flask was added **4a** (103 mg, 0.5 mmol), followed by 5 mL of dry toluene, then DMAP (92 mg, 0.75 mmol) and Ac_2O (77 mg, 0.75 mmol). The mixture was stirred at 80 °C for 24 h. After the same workup process as the preparation of **1a** and column chromatographic purification, pure **1b** (97 mg, 78%) was obtained as a colorless oil. **1b**:[19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.35−7.45 (m, 5H), 4.96 (s, 2H), 4.31 (q, J = 7.2 Hz, 2H), 2.11 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H).

Preparation of 8. An acetyl chloride (188 mg, 2.4 mmol) solution in 5 mL of dichloromethane was added dropwise to a mixture of **5a** (344 mg, 2 mmol) and pyridine (206 mg, 2.6 mmol) in 8 mL of dry dichloromethane at 0 °C. The temperature was kept for 5−10 min, and then the mixture was warmed to room temperature and continued to stir overnight. After the same workup process as the preparation of **1a** and column chromatographic purification, the product **8** (312 mg, 73%) was obtained as a colorless oil. **8**:[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (s, 1H), 5.75 (t, J = 1.0 Hz, 1H), 5.64 (dd, J = 7.8, 4.6 Hz, 1H), 4.26 (dq, J = 10.8, 7.1 Hz, 1H), 4.21 (dq, J = 10.8, 7.1 Hz, 1H), 2.08 (s, 3H), 1.58−1.80 (m, 2H), 1.26−1.46 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.3 Hz, 3H).

General Procedure for the DMAP-Catalyzed [3 + 2] Reaction between C_{60} and MBH Adducts (4a−4h) in the Presence of Ac_2O. To a 25 mL one-neck flask was sequentially added C_{60} (36.0 mg, 0.05 mmol), DMAP (18.3 mg, 0.15 mmol), BH adducts **4a**−**4h** (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, Ac_2O (15.3 mg, 0.15 mmol) was added and the mixture was stirred at 120 °C for 3−10 h. The solvent was evaporated in vacuo, and the residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60}. Subsequent elution with CS_2/toluene in the appropriate ratio afforded the [3 + 2] products **2a**−**2h**.

2a: Brown solid, 16.5 mg, 36%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 1.8 Hz, 1H), 7.76 (br, 1H), 7.64 (br, 1H), 7.49 (br, 1H), 7.39 (br, 1H), 7.31 (t, J = 7.4 Hz, 1H), 6.21 (d, J = 1.8 Hz, 1H), 4.36 (dq, J = 10.8, 7.2 Hz, 1H), 4.29 (dq, J = 10.8, 7.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.22 (C═O), 156.63, 154.14, 151.32, 151.14, 147.67, 147.56, 146.61, 146.53, 146.34 (2C), 146.27 (2C), 146.24, 146.21, 146.12, 145.99, 145.95, 145.88, 145.82, 145.74, 145.68, 145.65, 145.61, 145.53, 145.32 (2C), 145.22, 145.19, 144.83 (2C), 144.67, 144.65, 144.60, 144.43, 143.32, 143.29, 142.89, 142.83, 142.76, 142.74, 142.62, 142.41 (2C), 142.36, 142.28, 142.18, 142.17, 142.00, 141.99, 141.97, 141.93, 141.83, 141.25, 140.74, 140.53, 140.31, 139.56, 139.11, 137.02, 136.33, 135.72, 134.37, 129.20 (br, 2C, aryl C), 127.96 (2C, aryl C), 77.26 (sp^3-C of C_{60}), 74.86 (sp^3-C of C_{60}), 63.35, 61.34, 14.29; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; FT-IR (KBr) ν/cm^{-1} 2920, 2850, 1717, 1645, 1259, 1095, 1020, 802, 752, 698, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{72}H_{12}O_2$, 908.0837; found, 908.0816.

2b: Brown solid, 13.9 mg, 29%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 8.32 (br, 1H), 8.22 (br, 1H), 8.11 (s, 1H), 7.91 (br, 1H), 7.79 (br, 1H), 6.26 (d, J = 1.5 Hz, 1H), 4.24−4.36 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 162.93 (C═O), 155.47, 152.43, 150.29, 150.12, 148.10, 147.48, 147.40, 147.34, 146.41, 146.37, 146.19 (2C), 146.14, 146.11, 146.09, 146.05, 145.80 (2C), 145.59 (4C), 145.51, 145.44 (2C), 145.43, 145.38, 145.27, 145.19, 144.95, 144.43, 144.37 (3C), 144.22, 143.19, 143.16, 142.72, 142.71, 142.67, 142.61, 142.29, 142.14, 142.13, 142.08, 141.99, 141.96, 141.81 (2C), 141.75, 141.69, 141.67, 140.68, 140.56, 140.22, 139.60, 137.89, 136.43, 135.97, 135.70, 134.30, 128.36 (br, 2C), 124.18 (br, 2C), 77.06 (sp^3-C of C_{60}), 76.91 (sp^3-C of C_{60}), 62.79, 61.38, 14.34; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309.5, 430.5; FT-IR (KBr) ν/cm^{-1} 2920, 2850, 1714, 1652, 1514, 1342, 1263, 1226, 1096, 1022, 843, 702, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{72}H_{11}NO_4$, 953.0688; found, 953.0669.

2c: Brown solid, 15.5 mg, 33%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$−CS_2) δ 7.99 (s, 1H), 7.15−7.04 (m, 2H), 6.88−6.75 (m, 1H), 6.10−5.94 (m, 3H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 163.91 (C═O), 156.24, 153.72, 150.95, 150.70, 147.41, 147.32, 147.21, 146.38, 146.32, 146.10 (2C), 146.04 (2C), 146.02, 145.99, 145.79, 145.66, 145.64, 145.58, 145.54, 145.51, 145.43, 145.37, 145.28, 145.14, 145.09, 145.06 144.88, 144.51, 144.41, 144.36, 144.19, 143.12, 143.08, 142.70, 142.62, 142.57, 142.53, 142.44, 142.21, 142.18, 142.15, 142.06, 141.95, 141.93, 141.84, 141.79, 141.76 (2C), 141.61, 140.34, 140.16, 139.48, 138.58, 136.84, 136.04, 135.54, 134.71 (br), 134.05, 123.71 (br), 120.74 (br), 108.52 (br), 107.41 (br), 101.24, 76.78 (sp^3-C of C_{60}), 74.62 (sp^3-C of C_{60}), 62.85, 52.01; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 430.5; FT-IR (KBr) ν/cm^{-1} 2943, 2893, 1725, 1644, 1512, 1502, 1482, 1431, 1337, 1247, 1227, 1131, 1095, 1034, 928, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{72}H_{10}O_4$, 938.0597; found, 938.0586.

2d: Brown solid, 13.9 mg, 31%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.97 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 6.51 (d, J = 3.2 Hz, 1H), 6.36 (dd, J = 3.2, 1.9 Hz, 1H), 6.21 (d, J = 1.9 Hz, 1H), 4.38 (dq, J = 10.7, 7.1 Hz, 1H), 4.32 (dq, J = 10.7, 7.1 Hz, 1H), 1.37 (t, J =

dx.doi.org/10.1021/jo3025797 | J. Org. Chem. 2013, 78, 1163−1170

7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 163.11 (C═O), 155.50, 153.24, 152.80, 150.80, 150.58, 147.39, 147.28, 146.33, 146.29, 146.13, 146.07, 146.05, 146.03, 145.99, 145.97 (2C), 145.72, 145.66, 145.61, 145.59, 145.49 (2C), 145.39, 145.33, 145.23 (2C), 145.12, 145.07 (2C), 144.85 (2C), 144.52, 144.37, 144.33, 144.19, 143.06, 143.03, 142.69, 142.57, 142.55, 142.52, 142.41 (2C), 142.29, 142.20 (2C), 142.15, 142.04, 141.94, 141.90, 141.78 (2C), 141.76, 141.75, 141.55, 140.56, 140.31, 140.04, 139.34, 136.93, 136.27, 135.95, 135.52, 134.32, 110.94, 108.74, 76.61 (sp^3-C of C_{60}), 73.93 (sp^3-C of C_{60}), 61.12, 56.55, 14.42; UV−vis ($CHCl_3$) λ_{max}/nm 256.5, 310, 431; FT-IR (KBr) ν/cm^{-1} 2920, 2850, 1716, 1645, 1368, 1255, 1226, 1095, 1073, 1010, 738, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{70}H_{10}O_3$, 898.0630; found, 898.0647.

2e: Brown solid, 8.8 mg, 19%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.90 (d, J = 1.7 Hz, 1H), 7.41 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 15.5 Hz, 1H), 6.74 (dd, J = 15.5, 9.8 Hz, 1H), 5.68 (dd, J = 9.7, 1.7 Hz, 1H), 4.44 (dq, J = 10.8, 7.2 Hz, 1H), 4.38 (dq, J = 10.8, 7.2 Hz, 1H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 163.83 (C═O), 156.12, 153.20, 151.05, 150.81, 147.50, 147.41, 146.43, 146.40, 146.29, 146.22 (2C), 146.19, 146.16, 146.13, 146.10, 145.90, 145.86, 145.81, 145.75, 145.61 (2C), 145.50 (2C), 145.41, 145.34, 145.25, 145.22 (2C), 144.61, 144.54, 144.41, 144.30, 143.88 (3C), 143.24, 143.17, 142.75 (2C), 142.69, 142.62, 142.44, 142.32, 142.30, 142.27, 142.13, 142.11, 142.07 (2C), 141.94 (2C), 141.78, 141.73, 140.60, 140.49, 140.22, 139.93, 138.83, 136.67, 136.65, 136.11, 135.60, 134.25, 134.18, 129.25, 128.68 (2C), 128.02, 126.84 (2C), 76.98 (sp^3-C of C_{60}), 73.86 (sp^3-C of C_{60}), 61.24, 60.86, 14.51; UV−vis ($CHCl_3$) λ_{max}/nm 257.5, 310, 431; FT-IR (KBr) ν/cm^{-1} 2922, 2850, 1717, 1642, 1258, 1244, 1225, 1093, 959, 902, 745, 729, 690, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{74}H_{14}O_2$, 934.0994; found, 934.1005.

2f: Brown solid, 15.1 mg, 35%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.90 (d, J = 2.1 Hz, 1H), 7.65 (br, 2H), 7.48 (br, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.07 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 155.09, 152.03, 149.62, 148.96, 148.93 (2C), 148.87, 147.35, 147.25, 146.34, 146.28, 146.04 (3C), 146.00, 145.98, 145.92, 145.62, 145.53 (2C), 145.46, 145.38, 145.35, 145.31, 145.22 (2C), 145.17, 145.09, 145.06, 145.03, 144.45, 144.32, 144.28, 144.14, 144.10, 143.04, 143.02, 142.63, 142.57, 142.56, 142.51, 142.16, 142.08, 142.06, 141.94, 141.91, 141.84, 141.80,141.72, 141.67, 141.65 (2C), 141.56, 140.54, 140.32, 140.10, 139.44, 137.56, 136.47, 136.21, 135.32, 134.00, 129.44 (2C), 128.82 (2C), 119.22, 114.15, 73.58 (sp^3-C of C_{60}), 64.69; UV−vis ($CHCl_3$) λ_{max}/nm 256, 310.5, 430; FT-IR (KBr) ν/cm^{-1} 2920, 2850, 2223, 1511, 1453, 1428, 901, 883, 729, 705, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{70}H_7N$, 861.0578; found, 861.0590.

2g: Brown solid, 14.9 mg, 33%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.86 (d, J = 2.2 Hz, 1H), 7.10 (br, 2H), 6.86 (br, 1H), 6.01 (s, 2H), 5.98 (d, J = 1.7 Hz, 1H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 155.12, 152.07, 149.71, 148.98, 148.63 (3C), 148.04, 147.38, 147.28, 146.37, 146.31, 146.08, 146.06 (2C), 146.03, 146.01, 145.95, 145.64, 145.55 (2C), 145.46, 145.43, 145.39, 145.34, 145.35, 145.24, 145.20, 145.15, 145.09, 145.07, 144.47, 144.35, 144.33, 144.18, 144.14, 143.08, 143.04, 142.67, 142.59 (2C), 142.54, 142.20, 142.13, 142.09, 141.98, 141.94, 141.85 (2C), 141.77, 141.75, 141.70 (2C), 141.58, 140.56, 140.34, 140.14, 139.57, 136.53, 136.20, 135.39, 133.96, 131.30, 119.46, 114.12, 108.95 (br), 101.48, 76.84 (sp^3-C of C_{60}), 73.74 (sp^3-C of C_{60}), 64.54; UV−vis ($CHCl_3$) λ_{max}/nm 256.5, 310.5, 430; FT-IR (KBr) ν/cm^{-1} 2920, 2851, 2223, 1501, 1482, 1443, 1236, 1099, 1038, 928, 706, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{71}H_7NO_2$, 905.0477; found, 905.0471.

2h: Brown solid, 12.7 mg, 29%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.96 (d, J = 1.7 Hz, 1H), 7.61 (br, 2H), 7.42 (br, 1H), 7.36 (br, 1H), 7.27 (t, J = 7.4 Hz, 1H), 6.20 (d, J = 1.6 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 194.12 (C═O), 156.26, 153.81, 150.82, 150.71, 147.35, 147.29, 146.41, 146.37, 146.30, 146.07, 146.05, 146.01 (2C), 145.98, 145.96, 145.66, 145.60 (2C), 145.59, 145.53, 145.49 (2C), 145.40, 145.35, 145.26, 145.11, 145.05, 144.98, 144.86, 144.49, 144.40, 144.31, 144.11, 143.70 (2C), 143.10, 143.07, 142.68, 142.59, 142.55, 142.50, 142.43, 142.16 (2C), 142.09, 141.99, 141.90 (2C), 141.74 (2C), 141.73 (2C), 141.60, 140.87, 140.55, 140.33, 140.16, 139.40, 136.90, 136.14, 135.44, 134.00, 129.13 (br, 2C), 127.82 (2C), 74.33 (sp^3-C of C_{60}), 63.16, 27.96; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; FT-IR (KBr) ν/cm^{-1} 2919, 2850, 1679, 1622, 1423, 1359, 1261, 1221, 1093, 1021, 799, 702, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{71}H_{10}O$, 878.0732; found, 878.0719.

General Procedure for [4 + 2] Reaction between C_{60} and MBH Adducts (5a−5d) in the Presence of Ac_2O and DMAP. To a 25 mL one-neck flask was sequentially added C_{60} (36.0 mg, 0.05 mmol), DMAP (18.3 mg, 0.15 mmol), MBH adducts **5a−5d** (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, Ac_2O (15.3 mg, 0.15 mmol) was added and the mixture was stirred at 120 °C for 2−5 h. The solvent was evaporated in vacuo, and the residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60}. Subsequent elution with CS_2/toluene in the appropriate ratio afforded the [4 + 2] products **6a−6d**.

6a: Brown solid, 15.3 mg, 35%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.81 (br, 1H), 4.65 (d, J = 14.2 Hz, 1H), 4.33−4.43 (m, 2H), 4.12 (d, J = 13.9 Hz, 1H), 3.85 (d, J = 11.5 Hz, 1H), 2.81−2.89 (m, 1H), 2.26−2.29 (m, 1H), 1.46 (t, J = 7.3 Hz, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 164.67 (C═O), 157.09, 156.91, 153.88, 147.69, 147.56, 146.86, 146.62 (2C), 146.52 (2C), 146.40, 146.26 (3C), 146.23, 145.87, 145.84, 145.79 (2C), 145.59, 145.56, 145.49, 145.45 (4C), 145.40, 145.37, 145.23, 144.80, 144.75, 144.61 (2C), 143.14 (2C), 142.73, 142.71, 142.67 (2C), 142.24 (3C), 142.16, 142.15, 142.11, 142.10, 141.92, 141.79, 141.66, 141.49, 141.41, 140.39 (2C), 139.06, 138.94, 136.32, 135.81, 135.74, 135.05, 134.93, 70.06 (sp^3-C of C_{60}), 67.49 (sp^3-C of C_{60}), 61.18, 49.75, 39.42, 26.09, 14.57, 13.71; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 432.5; FT-IR (KBr) ν/cm^{-1} 2923, 2867, 1702, 1541, 1429, 1371, 1267, 1231, 1206, 1132, 1078, 730, 527; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{69}H_{14}O_2$, 874.0994; found, 874.0962.

6b: Brown solid, 16.1 mg, 38%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 8.01 (t, J = 5.8 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.36 (s, 2H), 4.19 (d, J = 5.8 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) (all 2C unless indicated) δ 164.72 (1C, C═O), 156.40, 156.30, 147.71 (1C), 147.66 (1C), 146.58, 146.53, 146.29, 146.26, 145.81, 145.57 (4C), 145.48 (4C), 145.34, 145.13, 144.76, 144.65, 143.15, 142.65, 142.62, 142.24, 142.20, 142.14, 142.05, 141.70, 141.66, 141.18 (1C), 140.28, 140.18, 136.16 (1C), 135.76, 135.58, 65.66 (1C, sp^3-C of C_{60}), 65.13 (1C, sp^3-C of C_{60}), 61.20 (1C), 41.21 (1C), 38.89 (1C), 14.56 (1C);

6c: Brown solid, 10.4 mg, 25%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-DMSO-d_6) δ 7.74 (s, 1H), 4.47 (d, J = 14.3 Hz, 1H), 4.29 (d, J = 14.3 Hz, 1H), 4.03−4.09 (m, 1H), 2.82−2.92 (m, 1H), 2.27−2.38 (m, 1H), 1.52 (t, J = 7.1 Hz, 3H); UV−vis ($CHCl_3$) λ_{max}/nm 256, 310, 431; FT-IR (KBr) ν/cm^{-1} 2955, 2925, 2869, 2219, 1513, 1454, 1428, 1184, 765, 572, 527; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{67}H_9N$, 827.0735; found, 827.0767.

6d: Brown solid, 14.8 mg, 35%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.69 (s, 1H), 4.78 (d, J = 12.4 Hz, 1H), 3.88−4.00 (m, 2H), 2.85−2.94 (m, 1H), 2.67 (s, 3H), 2.25−2.36 (m, 1H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 194.78 (C═O), 157.12, 156.92, 153.78, 147.73, 147.55, 146.80, 146.65, 146.64, 146.52, 146.49, 146.37, 146.29, 146.27 (3C), 145.86, 145.78, 145.67 (2C), 145.60, 145.56, 145.51, 145.46 (3C), 145.43 (2C), 145.39, 145.29, 144.84, 144.80, 144.58, 144.55, 143.49, 143.16, 143.15, 142.74, 142.72, 142.67 (2C), 142.26, 142.22 (2C), 142.17, 142.12, 142.10, 142.06, 141.91, 141.80, 141.70, 141.45, 141.43, 140.46, 140.44, 139.06, 138.95, 136.19, 135.90, 135.32, 134.95, 70.01 (sp^3-C of C_{60}), 67.32 (sp^3-C of C_{60}), 49.77, 37.57, 26.10, 24.95, 13.79; UV−vis ($CHCl_3$) λ_{max}/nm 255, 310, 431; FT-IR (KBr) ν/cm^{-1} 2956, 2922, 2851, 1668, 1511, 1427, 1376, 1264, 1182, 1084, 764, 527; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{68}H_{12}O$, 844.0888; found, 844.0859.

General Procedure for the *n*-Bu_3P-Catalyzed [3 + 2] Reaction between C_{60} and MBH Adducts 5a−5d in the Presence of Ac_2O and Na_2CO_3. To a 25 mL one-neck flask was sequentially added C_{60} (36.0 mg, 0.05 mmol), Na_2CO_3 (15.9 mg, 0.15 mmol), BH adducts **5a−5d** (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, Ac_2O (15.3 mg, 0.15 mmol) and *n*-Bu_3P (10.1 mg, 0.05 mmol) were added and the mixture was stirred at room temperature for the

dx.doi.org/10.1021/jo3025797 | J. Org. Chem. 2013, 78, 1163−1170

designated time. After completion of the reaction, a solution of I_2 (32 mg) in methanol (0.5 mL) was added and the mixture was stirred for another 5 min (***Caution!*** *Transform the n-Bu_3P to n-Bu_3P=O; avoid the further reaction at a higher temperature in the process of removing solvent*). The solvent was then evaporated in vacuo, and the residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60}. Subsequent elution elution with CS_2/toluene in the appropriate ratio afforded the major or exclusive [3 + 2] products **7a**−**7d**.

7a: Brown solid, 15.7 mg, 36%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.77 (d, J = 1.4 Hz, 1H), 5.02 (d, J = 7.4 Hz, 1H), 4.45−4.55 (m, 2H), 2.55−2.62 (m, 1H), 2.38−2.45 (m, 1H), 1.94−2.02 (m, 1H), 1.79−1.87 (m, 1H), 1.51 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 164.91 (C=O), 157.23, 153.20, 151.73, 151.67, 147.66, 147.54, 146.77, 146.59, 146.54, 146.52, 146.35, 146.33, 146.30 (2C), 146.28, 146.25, 146.04, 145.94, 145.87, 145.69, 145.67, 145.63, 145.61 (2C), 145.47, 145.34, 145.30, 145.09, 144.77, 144.66 (2C), 144.52, 143.42, 143.34, 143.03 (2C), 142.97, 142.85 (2C), 142.77, 142.69, 142.49, 142.47, 142.43, 142.31, 142.24, 142.21, 142.11, 142.05, 141.93 (2C), 141.90, 140.69, 140.64, 140.25, 139.44, 136.92, 136.66, 136.03, 134.23, 77.77 (sp^3-C of C_{60}), 73.77 (sp^3-C of C_{60}), 61.40, 56.66, 36.79, 21.21, 14.65, 14.57; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 431; FT-IR (KBr) ν/cm^{-1} 2922, 2864, 1714, 1643, 1241, 1224, 1130, 1087, 902, 729, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{69}H_{14}O_2$, 874.0994; found, 874.1005.

7b: Brown solid, 16.9 mg, 40%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.77 (d, J = 1.7 Hz, 1H), 5.02 (qd, J = 7.2, 1.6 Hz, 1H), 4.42−4.52 (m, 2H), 2.07 (d, J = 7.3 Hz, 3H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 164.11 (C=O), 156.63, 153.32, 151.44, 151.24, 147.50, 147.40, 146.43, 146.39, 146.36, 146.31, 146.22, 146.17 (2C), 146.13 (2C), 145.99, 145.88, 145.84, 145.77, 145.57 (2C), 145.51 (2C), 145.41, 145.35, 145.21 (3C), 144.63, 144.54, 144.45, 144.36, 143.28, 143.20, 142.80, 142.75 (4C), 142.69, 142.63, 142.52, 142.30, 142.29 (2C), 142.22, 142.13, 142.08 (2C), 141.99, 141.82, 141.76 (2C), 141.25, 140.59, 140.53, 140.20, 139.82, 136.60, 136.18, 136.04, 134.10, 73.38 (sp^3-C of C_{60}), 61.20, 51.95, 21.32, 14.59; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 430.5; FT-IR (KBr) ν/cm^{-1} 2922, 2864, 1714, 1509, 1258, 1241, 1224, 1131, 765, 729, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{67}H_{10}O_2$, 846.0681; found, 846.0699.

7c: Brown solid, 12.4 mg, 30%, mp > 300 °C. ^{1}H NMR (500 MHz, CS_2-DMSO-d_6) δ 7.59 (br, 1H), 4.78−4.86 (m, 1H), 2.44−2.56 (m, 1H), 2.33−2.43 (m, 1H), 2.05−2.17 (m, 1H), 1.92−2.02 (m, 1H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) δ 154.92, 150.52, 149.58, 149.12, 146.74 (2C), 146.54, 146.40, 145.52, 145.47, 145.45, 145.34, 145.26 (2C), 145.22, 145.20, 145.18, 144.87, 144.80 (2C), 144.78, 144.72, 144.68, 144.55 (2C), 144.53, 144.49, 144.36, 144.26, 143.76, 143.54 (2C), 143.45 (2C), 142.33, 142.26, 142.18, 141.89, 141.85, 141.80, 141.74, 141.43, 141.38, 141.34, 141.20 (2C), 141.15, 141.13, 141.07. 140.97, 140.88, 140.86, 140.82, 139.61 (2C), 139.20, 138.57, 135.43, 135.34, 135.23, 133.25, 120.15, 114.10 (CN), 76.84 (sp^3-C of C_{60}), 71.45 (sp^3-C of C_{60}), 57.35, 36.94, 20.92, 13.94; UV−vis ($CHCl_3$) λ_{max}/nm 256, 310, 431; FT-IR (KBr) ν/cm^{-1} 2953, 2921, 2853, 2216, 1511, 1461, 1428, 1183, 1096, 883, 767, 574, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{67}H_9N$, 827.0735; found, 827.0728.

7d: Brown solid, 15.6 mg, 37%, mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.68 (s, 1H), 5.02−5.06 (m, 1H), 2.75 (s, 3H), 2.49−2.57 (m, 1H), 2.28−2.37 (m, 1H), 1.89−2.00 (m, 1H), 1.65−1.75 (m, 1H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 195.39 (C=O), 156.89, 152.98, 151.23, 151.13, 148.20, 147.34, 147.27, 146.48, 146.36, 146.30, 146.24, 146.08 (2C), 146.01 (2C), 145.98, 145.89, 145.70, 145.61, 145.47, 145.42, 145.39 (3C), 145.34, 145.23, 145.06, 144.78, 144.56, 144.42, 144.35, 144.19, 143.18, 143.10, 142.75, 142.69 (2C), 142.62 (2C), 142.52, 142.49, 142.24 (2C), 142.14, 142.01, 141.95, 141.92, 141.84 (2C), 141.68, 141.66 (2C), 140.47 (2C), 140.11, 139.27, 136.82, 136.30, 135.89, 133.81, 77.80 (sp^3-C of C_{60}), 73.20 (sp^3-C of C_{60}), 56.57, 36.24, 27.69, 21.27, 14.54; UV−vis ($CHCl_3$) λ_{max}/nm 256, 310, 431; FT-IR (KBr) ν/cm^{-1} 2950, 2920, 2852, 1673, 1629, 1507, 1426, 1360, 1220, 1183, 1083, 870, 766, 729, 526; HRMS (MALDI-FTMS) m/z [M$^+$] Calcd for $C_{68}H_{12}O$, 844.0888; found, 844.0871.

General Procedure for Phosphine-Catalyzed Reaction between C_{60} and Acetyl-Modified MBH Adduct 8. To a 25 mL one-neck flask were sequentially added C_{60} (36.0 mg, 0.05 mmol), **8** (0.15 mmol), and 16 mL of dry toluene. After ultrasonic dissolving, phosphine catalyst (PPh_3, 0.005 mmol; or n-Bu_3P, 0.005−0.05 mmol) was added and the mixture was stirred at 120 °C or room temperature for the designated time. The solvent was evaporated in vacuo, and the residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60}. Subsequent elution with CS_2/toluene in the appropriate ratio afforded the [3 + 2] products **7a** and [4 + 2] products **6a**. (When n-Bu_3P was used, the same workup process was applied as that of the one-step reaction mentioned above.)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of **1a**, **1b**, **2a**−**2h**, **6a**−**6d**, **7a**−**7d**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for financial support from the National Natural Science Foundation of China (Nos. 20902039 and 21202011) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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