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Monoalkylation of C_{60} and C_{70} with Zn and Active Alkyl Bromides

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We report a convenient and simple solution-phase electron-transfer reaction of C_{60} with zinc and α-bromoacetonitrile, α-bromo acetate esters, allyl bromide, benzyl bromide and α-bromo ketones in DMF, with which different types of monoalkylated C_{60} derivatives can be prepared. When this method is employed with C_{70}, 2-carbomethoxymethyl-1,2-dihydro[70]fullerene (isomer **5a**) is produced as one of the two 1,2-monoalkylated C_{70} isomers, together with the first 5,6-monoalkylated C_{70} derivative.

Introduction

Since C_{60} was first isolated and produced in bulk quantities,[1,2] chemists have been attracted by its interesting chemistry[3−10] as well as by potential applications.[4,11−14]

C_{60} reacts as an electrophilic molecule with highly strained double bonds.[15−17] Relief of strain is the essential driving force for most of the reactions known to proceed with fullerenes.[17] Reactions that have been successfully employed on C_{60}[3−10] include nucleophilic additions, Diels−Alder, [1,3]-dipolar, and other types of cycloadditions, oxidations, halogenations, addition of carbenes and nitrenes,[18] hydrogenations,[19,20] organo-transition-metal reactions,[21] and others.[3−10]

Due to complexities from the lower symmetry (D_{5h}), there are significantly fewer reports of chemical reactions of C_{70} than there are of C_{60}.[3−8,22] However, hydrogenation,[23−25] fulleroid synthesis,[26] azafulleroid synthesis,[27] oxidations,[28−30] cycloaddition,[31−37] chlorination,[38] arylation,[39,40] reactions with organometallic reagents,[41] and addition of nucleophiles[42−45] have been reported. Among these, monoalkylation is one of the most important reactions, as versatile synthetic intermediates are formed.

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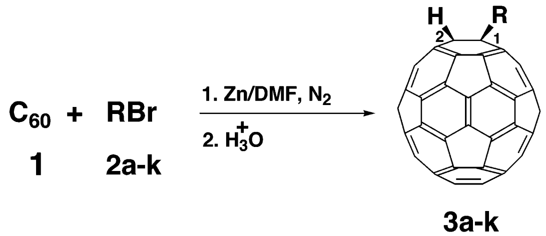
There are several methods for preparation of monoalkylated C_{60} derivatives, including addition of nucleophilic organometallic reagents to C_{60},[45−51] nucleophilic additions of C_{60}^{2-} or $C_{60}H^-$ derived chemically from C_{60},[52,53,54] from $C_{60}H_2$,[44] and photoinduced electron transfer (PET) radical additions.[45,55−62] However, monoalkylation of anions from $C_{60}H_2$ or by the reaction of C_{60} with organometallic reagents can be difficult to control and sometimes proceeds rapidly to dialkylated or polyalkylated adducts.[44,50] Nucleophilic addition reactions have also been employed for the preparation of monoalkylation of C_{70}.[42−45] In these cases, the structure of the monoalkylated C_{70} derivative has not been unambiguously elucidated due to the limited amount available, the complex reaction mixtures, the poor solubility, the difficulty in crystallization and the lack of well-characterized analogues for comparison of chemical shifts in the ^{1}H NMR.

We are interested in preparation of monoalkylfullerenes through alkylation of anions derived from $C_{60}H_2$ and $C_{70}H_2$,[44] as well as in direct addition of nucleophilic reagents to C_{60} and C_{70}. In this paper, we report a convenient solution-phase method for the monoalkylation of C_{60} (Scheme 1) and C_{70} (Scheme 2), by reaction with Zn and alkyl bromides.[63,64] We also report the first elucidation of the structures of two monoalkylated C_{70} derivatives. These reactions provide an approach to the synthesis of fullerene derivatives bearing a variety of functional groups, compounds that can be further modified for specific applications.

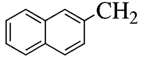
Discussion

Production of fullerene anions is commonly accomplished by dissolving metal reductions,[65] including reductions with zinc.[66] Electrons can be transferred from alkali metals (e.g., K, Na) to fullerenes,[3−10] and the resulting anions can then be alkylated to produce monoalkylated C_{60} derivatives.[52] In our initial studies on monoalkylation of C_{60} using Zn and alkyl halides, we found that almost no reaction occurred when toluene was used as solvent, even when the mixture was heated. However, when DMF was used as solvent, the reaction proceeded smoothly at room temperature. With control of reaction temperature and time, monoalkylated products (**3a**−**k**) could be obtained in isolated yields that ranged from 6% to 45% (10−78% yield when adjusted for the unreacted C_{60}). Some examples, such as the reactions using phenyl α-bromoacetate, allyl bromide, or benzyl bromide, proceeded very rapidly and the reaction had to be carefully monitored by TLC or by HPLC to avoid multiple additions.

SCHEME 1



3a-k

3a: R= CH_2CN
3b: R= CH_2CO_2Me
3c: R= CH_2CO_2Et
3d: R= $CH_2CO_2CH_2Ph$
3e: R= CH_2CO_2Ph
3f: R= $CH_2CH{=}CH_2$
3g: R= CH_2Ph
3h: R= CH_2COPh
3i: R= CH_2COBu-t
3j: R= $CH_2CH{=}CHCO_2Me$
3k: R = 

We extended the study to a number of alkylating reagents and found that active alkylation reagents, such as α-bromoacetonitrile, α-bromoacetate esters, allyl bromide, benzyl bromide, and α-bromo ketones, can react with C_{60} successfully in the presence of zinc. Some less reactive reagents, such as α-chloroacetate esters, α-substituted-α-bromoacetate esters, α-bromo-*n*-butane, 1-iodobutane, and (2-iodoethyl)benzene failed to react with C_{60}, even when the corresponding zinc cuprates[20] were used at elevated temperature.

As with most derivatives of C_{60}, the solubilities of the monoalkylated products are reasonable in toluene and CS_2, except for **3a**. Compound **3a** has limited solubility in CS_2, but sufficient material could be dissolved in 1,2-dichlorobenzene-d_4 to permit measurement of the ^{13}C NMR spectrum. Besides CS_2 and toluene, most of the products are slightly soluble in solvents such as THF, chloroform, dioxane, etc., but almost insoluble in ether, DMF and acetone. The products are very stable in air at room temperature; e.g., **3b** can stand in air for several months.[67]

It should be noted that because the organozinc reagents derived from α-bromo ketones self-condense in the presence of Zn, the heterocoupling reactions of organozinc reagents derived from α-bromo ketones and Zn with other

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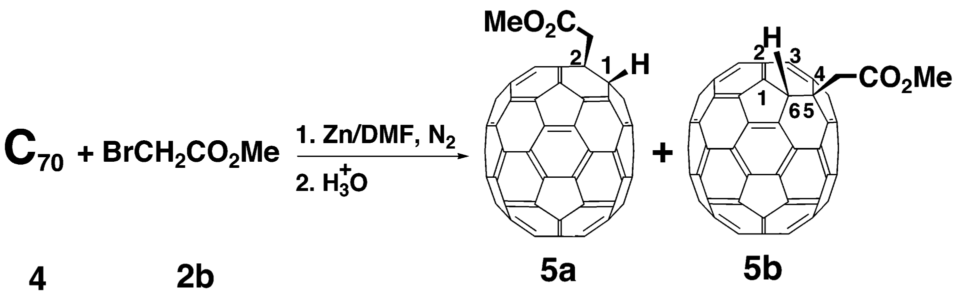
(67) It should be noted when air was passed through the solution of **3b** in toluene at room temperature a trace of C_{60} appeared and also a small amount of insoluble solid appeared, although most of the sample survived.

SCHEME 2



carbonyl compounds have been rarely reported.[63,64] Under the conditions used in this study, the reactions of α-bromo ketones, Zn, and C_{60} proceeded smoothly. All of the α-bromo ketone (including the excess reagent) was consumed, and the reaction proceeded to completion without formation of products from multiple additions. This is unlike the reactions of alkyl halides such as allyl bromide or benzyl bromide, in which multiple additions occur over time. These results are consistent with a competing reaction between the α-bromo ketone and its corresponding organozinc reagent, but these are slow relative to the alkylation of C_{60}.

Wang has reported[47] an example of a solid-phase reaction of ethyl bromoacetate, Zn, and C_{60}, a reaction that is considered to be a Reformatsky reaction.[63,64] For the solution-state reaction studied in our work, we also anticipated a Reformatsky reaction. However when a preformed Reformatsky reagent was added to C_{60}, no reaction was observed. We found that if the alkylating agent was omitted and water was added after 1 h, $C_{60}H_2$ was obtained in 50% yield (by HPLC).[68] Based on these results, we believe that the mechanism of the monoalkylation reactions involves an electron-transfer reduction of the fullerene, rather than formation and addition of an organozinc reagent.

^{1}H, ^{13}C NMR, and UV−vis of Compounds 3a−k. A combination of ^{1}H and ^{13}C NMR, together with UV−vis spectroscopy, was used to assign the structure of compounds **3a**−**k**. For monoalkylated C_{60} derivatives (**3b**, for example), the chemical shift of the proton on the fullerene core is shifted downfield to 6.80 ppm, and the methylene group directly connected the fullerene core appears as a singlet at 4.47 ppm, indicating that the two protons in the methylene group are in the same chemical environment. In the ^{13}C NMR, we observe 30 resonances for the C_{60} core (including two sp^2 carbons of single intensity, two sp^3 carbons of single intensity and two sp^2 carbons of 4-fold intensity (due to the superposition of two lines of 2-fold intensity)). These data confirm that the structure is a 1,2-isomer with C_s symmetry.[69] The UV−vis spec-

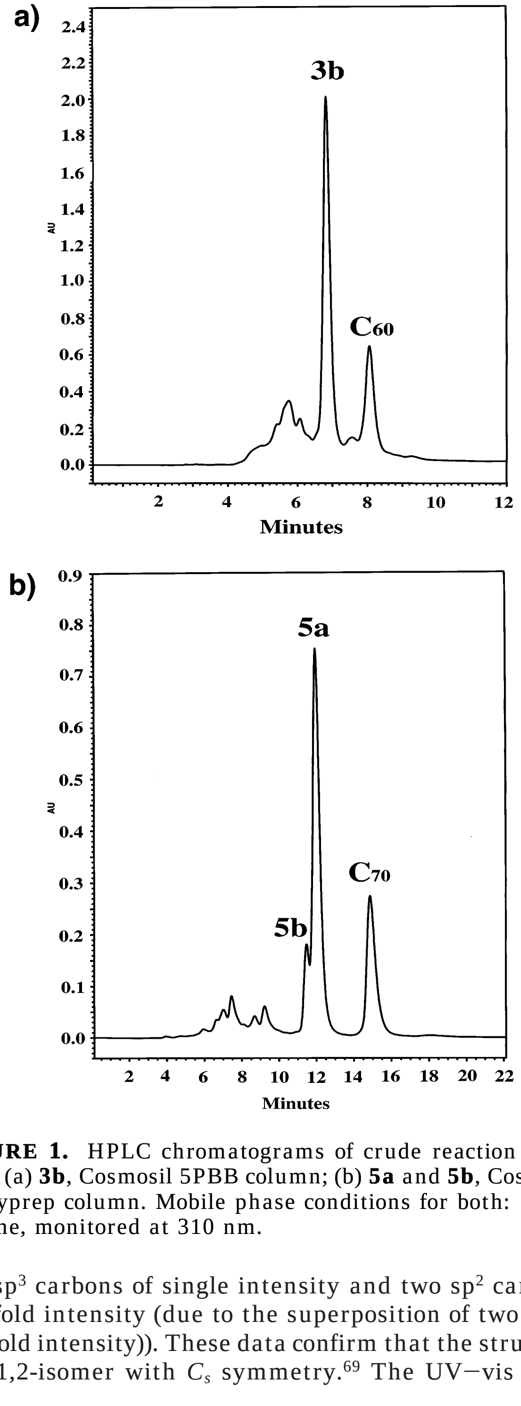


FIGURE 1. HPLC chromatograms of crude reaction products: (a) **3b**, Cosmosil 5PBB column; (b) **5a** and **5b**, Cosmosil Buckyprep column. Mobile phase conditions for both: 100% toluene, monitored at 310 nm.

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[68] (a) Control experiment one: C_{60} and Zn dust (activated by the method used in preparation of monoalkylated C_{60} derivatives) were mixed and stirred at room temperature under N_2. After 5 h, the black solution was decanted to toluene and H_2O and worked up as in preparation of monoalkylated C_{60} derivatives. The combination of HPLC, UV−vis, and ^{1}H NMR confirmed the production of 1,2-$C_{60}H_2$ with a yield of 50%, together with some $C_{60}H_4$ and higher hydrogenated adducts. (b) Control experiment two: A mixture of Zn (pretreated as before) and methyl bromoacetate was stirred at room temperature under N_2 for 1 h, and the solution was decanted to another two predried flasks, the volume of the solution in these two flasks was same. In one of these two flasks, C_{60} was added and the mixture was stirred at room temperature under N_2. No reaction was detected even after several days. In the other flask, 2,3-dimethoxybenzaldehyde was added and the mixture was stirred under N_2 for 4 h, after workup and purification with silica gel column, the expected Reformatsky-type product was obtained: ^{1}H NMR of the product ($CDCl_3$) (ppm) 2.72 (q, 1H), 2.73 (q, 1H), 3.41 (br, 1H), 3.69 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 5.35 (q, 1H), 6.84 (q, 1H), 6.99−7.06 (m, 2H).

[69] The fullerene core numbering system used herein is the "trivial" system described in: Powell, W. H.; Cozzi, F.; Moss, G. P.; Thilgen, C.; Hwu, R. J.-R.; Yerin, A. *Pure Appl. Chem.* **2002**, *74*, 629−695.

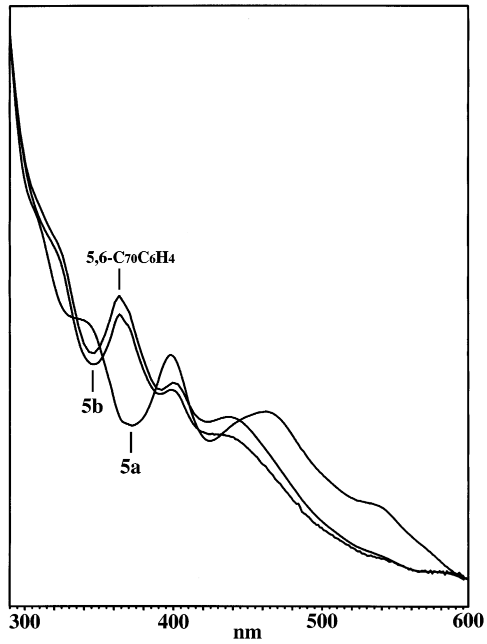


FIGURE 2. Absorption spectra of **5a** and **5b**.

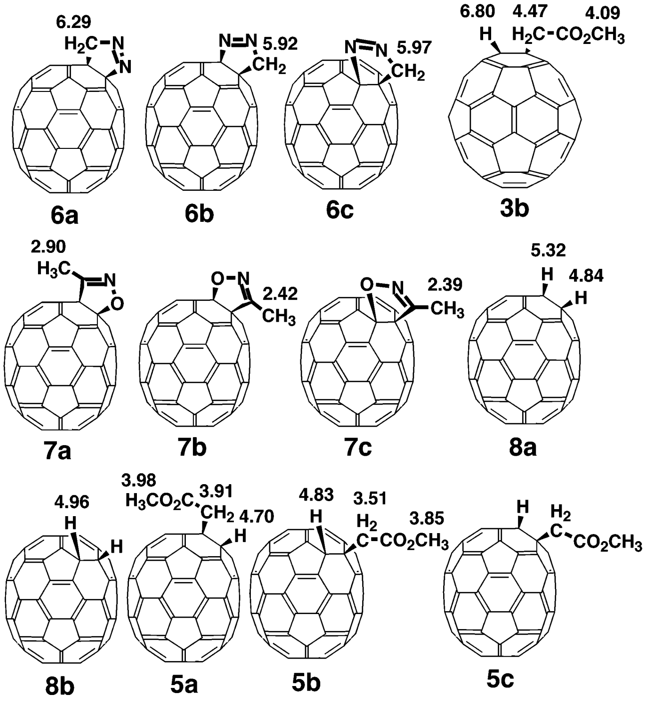
trum is also consistent, displaying a peak at 434 nm, characteristic of 1,2-adducts of C_{60}.[45]

As expected for C_{70}, the most reactive site toward alkylation is the strained C1−C2 bond, and in most examples we studied, the second more reactive one is the C5−C6-bond. In the reaction of methyl bromoacetate, Zn and C_{70}, two isomeric monoadducts were produced and isolated in a ratio of 9:1 by HPLC (Figure 1). The major isomer was identified as the 1,2-isomer (**5a**) and the minor isomer was identified as the 5,6-isomer (**5b**) by UV−vis (Figure 2) and NMR spectroscopy.

^{1}H and ^{13}C NMR and UV−vis of Compounds 5a and 5b. A combination of ^{1}H and ^{13}C NMR, together with UV−vis spectra, was also used to assign the structure of compounds **5a** and **5b**. For isomer **5b** (Scheme 2), the chemical shift of the proton on C_{70} is 4.83 ppm, and the methyl ester appeared as a singlet at 3.85 ppm. The methylene group showed an AB pattern with resonances at 3.56 and 3.46 ppm and a coupling constant of 16 Hz. The absorption spectrum of **5b** is like that of other 5,6-isomers of C_{70} adducts (Figure 2).[32] There are 62 resonances for the C_{70} core in the ^{13}C spectrum of **5b** (including two sp^3 carbon resonances of single intensity, 8 sp^2 carbon resonances of double intensity, and 52 sp^2 carbon resonances of single intensity) and two sp^3 nonfullerene (upfield) carbon resonances, together with the carbonyl resonance (169.96 ppm). The data indicate the symmetry is C_1. All of the data above are consistent with the assignment of **5b** as the 5,6-isomer. Addition to the C5−C6 bond has been reported often in the literature and is established as the second most reactive bond in C_{70}.[29,30,32,35,36]

In the ^{1}H NMR of isomer **5a** (Scheme 2), the chemical shift of the proton on the C_{70} core is 4.70 ppm, which is significantly shielded relative to the fullerene-bound proton in **3b**. The resonances of the protons in the methylene and methyl groups of **5a** appear as singlets at 3.91 and 3.98 ppm, respectively. In the ^{13}C NMR spectrum of **5a**, there are 33 resonances for the C_{70} core (including two sp^3 carbon resonances of single intensity, two sp^2 carbon resonances of single intensity, two resonances of 4-fold intensity, and one resonance of 6-fold intensity resulting from the superposition of several resonances), together with two resonances for two sp^3 nonfullerene carbons and the carbonyl group resonance (170.05 ppm). The UV−vis spectrum of **5a** is almost identical to that of 1,2-$C_{70}H_2$. All these data confirm that isomer **5a** results from addition to the C1−C2 bond.

SCHEME 3. Chemical Shifts (ppm) of Protons in Several Types of Fullerene Derivatives



There are two possible orientations for addition to the C1−C2 bond, **5a** and **5c**. Generally, protons over the pole of C_{70} have higher chemical shifts than others over the less pyramidalized carbons; that is, the protons at C-2 have significantly higher chemical shifts than at C-1. This trend holds in the case of protons directly connected to the fullerene cores (**8a**), of methylene groups directly connected to the fullerene cores (**6a** and **6b**), and of methyl groups indirectly connected to the fullerene cores (**7a** and **7b**): $\Delta\delta_{\mathrm{CH2}}$**6a**−**6b** $= 0.37$ ppm,[31] $\Delta\delta_{\mathrm{CH3}}$**7a**−**7b** $= 0.48$ ppm,[35] $\Delta\delta_{\mathrm{H}}$**8a**$H_2$−**8a**$H_1 = 0.14$ ppm.[23,25,70] The chemical shifts of protons at C1 and C5 are typically very similar due to their similar environments ($\Delta\delta_{\mathrm{CH2}}$**6b**−**6c** $= -0.05$ ppm, $\Delta\delta_{\mathrm{CH2}}$**7b**−**7c** $= 0.03$ ppm, $\Delta\delta_{\mathrm{H}}$**8a**$H_1$−**8b** $= -0.12$ ppm). In our case, there is only a small difference between the chemical shifts of protons directly connected to C_{70} cores in **5a** and **5b** ($\Delta\delta_{\mathrm{H}}$**5a**−**5b** $= -0.13$ ppm), but a large difference between the chemical shifts of protons at methylene groups in **5a** and **5b** ($\Delta\delta_{\mathrm{CH2}}$**5a**−**5b** $= 0.40$ ppm[71]). Based on this analysis, we believe the 1,2-isomer we obtained is **5a**, in which the proton is at C1 and CH_2CO_2Me group is at C2 (Scheme 3).

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(70) H1 and H2 represent the protons on positions 1 and 2 of C_{70}, respectively.

(71) The chemical shift values of methylene groups in **5b** and **6c** are the averaged values of the geminal protons.

Conclusions

To the best of our knowledge, this is the first report of solution-phase reactions of C_{60} and C_{70} with Zn and alkylating agents. A number of different types of monoalkylated C_{60} derivatives can be conveniently and simply prepared. With further manipulations, additional types of homo- and hetero-dialkylated derivatives or other types of derivatives can be prepared. By comparison of the ^{1}H NMR spectrum with other literature examples, the structure of isomer **5a** is assigned. Also in this paper, the first 5,6-isomer of monoalkylated C_{70} was produced, separated, and characterized.

Experimental Section

C_{60} (99.5+%) and C_{70} (98+%) were purchased from MER Corp. HPLC was performed using a Cosmosil 5PBB (10 mm × 250 mm) (100% toluene as the mobile phase) semipreparative column and/or Cosmosil Buckyprep (10 mm × 250 mm) (100% toluene as the mobile phase) semipreparative column. ^{1}H and ^{13}C NMR were measured at 400 and 100 MHz, respectively, on a 400 MHz instrument and, unless otherwise noted, using 75% CS_2 and 25% $CDCl_3$ as solvents and using $CHCl_3$ as the reference. UV−vis spectra were recorded during HPLC analysis with a Waters 996 PDA detector. Mass spectral data were obtained by negative-ion FAB, using nitrobenzyl alcohol (NBA) as matrix.

General Experimental Procedure. Into a 100 mL two-neck flask were added C_{60} (144 mg, 0.20 mmol),[72] the alkyl halide (5.0 mmol), and 40 mL of DMF. Under a N_2 flow, the mixture was stirred vigorously and heated to 50 °C (oil-bath temperature), and then Zn dust (0.65 g, 10.0 mmol, having been successively washed with 1 × 2 mL 3% HCl, 3 × 5 mL distilled H_2O, 2 × 5 mL THF, and 1 × 5 mL DMF) was rinsed into the reaction mixture with 2 mL of DMF. The resulting mixture was stirred vigorously, and the color turned to deep black. After more specific time (TLC monitoring), the mixture was poured into 200 mL of H_2O containing 4 mL of AcOH, and 300 mL of toluene was added. The mixture was shaken, the layers were separated, and the upper (toluene) layer was further washed with H_2O (2 × 150 mL) and dried overnight with anhydrous Na_2SO_4. After being filtered and concentrated, the concentrated solution (∼15 mL, or more, depending on the solubility of the products) was applied to a silica gel column and eluted with toluene/hexane (1:9) to produce a band composed of unreacted C_{60} and then eluted with 100% toluene to obtain a second fraction that contained the alkylated products. The second fraction was separated by HPLC to obtain the purified products. The HPLC chromatograms of C_{60} and C_{70} reactions are shown in Figure 1, and the UV spectra of the two isomers (**5a** and **5b**) of C_{70} derivatives are shown in Figure 2.

Characterization data is presented here as **compound** (reaction temperature, reaction time, yield (% purified, % yield based on the reacted C_{60} and C_{70}): ^{1}H and ^{13}C NMR, MS and UV−vis (λ_{max}, nm) spectra.

1-Cyanomethyl-1,2-dihydro[60]fullerene (3a) (50 °C, 1 h, 18%, 34%): ^{1}H NMR 4.47 (s, 2H), 6.59 (s, 1H); ^{13}C NMR (1,2-dichlorobenzene-*d*$_4$, with benzene as the reference) 35.35 (1C), 58.99 (1C), 60.78 (1C), 135.82 (2C), 136.68 (2C), 140.06 (2C), 140.18 (2C), 141.28 (2C), 141.55 (4C), 141.79 (2C), 141.94 (2C), 142.05 (2C), 142.42 (2C), 142.48 (2C), 143.02 (2C), 144.22 (2C), 144.58 (2C), 145.08 (2C), 145.20 (2C), 145.33 (2C), 145.38 (2C), 145.49 (2C), 145.70 (2C), 146.07 (2C), 146.13 (2C), 146.27 (2C), 146.32 (2C), 146.38 (2C), 147.18 (1C), 147.46 (1C), 151.24 (2C), 151.87 (2C), 192.34 (1C) MS: 720.3 (100), 761.3 (70%) (M$^-$); UV−vis 323.1, 432.0.

Methyl ([60]fulleren-1(2*H*)-yl)acetate (3b) (1 h, 50 °C, 45%, 78%): ^{1}H NMR 4.09 (s, 3H), 4.47 (s, 2H), 6.80 (s, 1H); ^{13}C NMR: 49.43 (1C), 52.36 (1C), 59.41 (1C), 61.18 (1C), 136.54 (2C), 136.89 (2C), 140.32 (2C), 140.40 (2C), 141.76 (4C), 141.77 (2C), 142.08 (2C), 142.21 (2C), 142.31 (2C), 142.68 (2C), 142.72 (2C), 143.36 (2C), 144.62 (2C), 144.92 (2C), 145.46 (2C), 145.55 (4C), 145.72 (2C), 145.77 (2C), 145.93 (2C), 146.30 (2C), 146.33 (2C), 146.48 (2C), 146.55 (2C), 147.05 (2C), 147.38 (1C), 147.65 (1C), 153.48 (2C), 153.98 (2C), 170.48 (1C); MS 719.9 (100), 794.9 (35) (M$^-$); UV−vis 307.7, 327.9, 434.5.

Ethyl ([60]fulleren-1(2*H*)-yl)acetate (3c)[47,60] (1 h, 50 °C, 30%, 51%): ^{1}H NMR 1.58 (t, 3H), 4.45 (2H), 4.56 (q, 2H), 6.82 (s, 1H); ^{13}C NMR 14.94 (1C), 49.61 (1C), 59.41 (1C), 61.24 (1C), 61.70 (1C), 136.57 (2C), 136.88 (2C), 140.31 (2C), 140.38 (2C), 141.76 (6C), 142.07 (2C), 142.20 (2C), 142.30 (2C), 142.66 (2C), 142.71 (2C), 143.36 (2C), 144.63 (2C), 144.91 (2C), 145.45 (2C), 145.53 (2C), 145.54 (2C), 145.74 (4C), 145.93 (2C), 146.28 (2C), 146.31 (2C), 146.47 (2C), 146.53 (2C), 147.06 (2C), 147.37 (1C), 147.63 (1C), 153.53 (2C), 154.11 (2C), 169.78 (1C); MS 720.2 (100), 808.2 (75) (M$^-$); UV−vis 306.5, 326.7, 433.2.

Benzyl ([60]fulleren-1(2*H*)-yl))acetate (3d) (50 °C, 40 min, 20%, 40%): ^{1}H NMR 4.47 (s, 2H), 5.50 (s, 2H), 6.78 (s, 1H), 7.33−7.43 (m, 3H), 7.51−7.56 (m, 2H); ^{13}C NMR 49.18 (1C), 58.89 (1C), 60.85 (1C), 67.09 (1C), 128.48 (1C), 128.55 (2C), 128.74 (2C), 135.10 (2C), 136.15 (2C), 136.50 (2C), 139.89 (2C), 139.96 (2C), 141.36 (4C), 141.67 (2C), 141.81 (2C), 141.89 (2C), 142.27 (2C), 142.31 (2C), 142.97 (2C), 144.23 (2C), 144.52 (2C), 145.06 (2C), 145.13 (4C), 145.36 (4C), 145.53 (2C), 145.89 (2C), 145.93 (3C), 146.07 (2C), 146.14 (2C), 146.64 (2C), 146.99 (1C),147.24 (1C),153.00 (2C),153.52 (2C),169.41 (1C); MS 720.3 (100), 870.2 (75) (M$^-$); UV−vis 306.5, 327.9, 434.2.

Phenyl ([60]fulleren-1(2*H*)-yl)acetate (3e) (room temperature, 1 h, 11%, 47%): ^{1}H NMR 4.71 (s,2H), 6.89 (s,1H), 7.32−7.39 (m,3H), 7.47−7.52 (m,2H); ^{13}C NMR 49.74 (1C), 59.29 (1C), 61.18 (1C), 121.73 (1C), 126.36 (2C), 129.73 (2C), 136.50 (2C), 136.94 (2C), 140.37 (2C), 140.44 (2C), 141.75 (2C), 141.76 (2C), 141.80 (2C), 142.08 (2C), 142.21 (2C), 142.31 (2C), 142.69 (2C), 142.74 (2C), 143.37 (2C), 144.61 (2C), 144.91 (2C), 145.47 (2C), 145.57 (4C), 145.67 (2C), 145.83 (2C), 145.92 (2C), 146.30 (2C), 146.34 (2C), 146.49 (2C), 146.57 (2C), 147.00 (2C), 147.39 (1C), 147.66 (1C), 150.65 (1C), 153.28 (2C), 153.65 (2C), 168.36 (1C); MS 720.0 (100), 856.0 (20) (M$^-$); UV−vis 307.7, 326.7, 433.2.

1-Allyl-1,2-dihydro[60]fullerene (3f) (50 °C, 1 h, 19%, 37%): ^{1}H NMR 4.21−4.24 (dt, 2H), 5.80−5.84 (dp, 1H), 5.94−6.00 (dq, 1H), 6.55 (s, 1H), 6.82−6.93 (m, 1H); ^{13}C NMR 51.31 (1C), 58.73 (1C), 64.38 (1C), 121.88 (1C), 133.53 (2C), 136.22 (2C), 136.47 (2C), 140.36 (2C), 140.40 (2C), 141.76 (2C), 141.77 (2C), 142.03 (2C), 142.08 (2C), 142.15 (2C), 142.33 (2C), 142.68 (4C), 143.37 (2C), 144.68 (2C), 144.82 (2C), 145.48 (2C), 145.50 (1C), 145.57 (2C), 145.65 (2C), 145.89 (2C), 146.23 (2C), 146.28 (2C), 146.33 (2C), 146.49 (2C), 146.51 (2C), 147.09 (2C), 147.38 (1C), 147.53 (1C), 153.84 (2C), 155.43 (2C); MS 720.3 (100), 762.3 (8) (M$^-$); UV−vis 305.3, 325.5, 433.2.

1-Benzyl-1,2-dihydro[60]fullerene (3g)[52,73] (35 °C, 30 min, 19%, 36%): ^{1}H NMR 4.79 (s, 2H), 6.65 (1H), 7.42−7.56 (m, 3H), 7.80−7.84 (d, 2H); ^{13}C NMR 53.32 (1C), 59.24 (1C), 65.92 (1C), 127.96 (1C), 128.94 (2C), 131.50 (2C), 135.78 (2C), 136.16 (2C), 136.43 (2C), 140.07 (2C), 140.33 (2C), 141.68 (2C), 141.75 (2C), 141.99 (2C), 142.07 (2C), 142.13 (2C), 142.27(2C), 142.66 (4C), 143.33 (2C), 144.65 (2C), 144.79 (2C), 145.46 (4C), 145.54 (2C), 145.59 (2C), 145.86 (2C), 146.26 (2C), 146.33 (2C), 146.36 (2C), 146.47(1C), 146.50 (2C), 147.00 (2C), 147.38 (1C), 147.53 (1C), 153.82 (2C), 155.25 (2C); MS 720.2 (100), 812.2 (45) (M$^-$); UV−vis 305.3, 326.7, 434.5.

([60]Fulleren-1(2*H*)-yl)acetophenone (3h) (50 °C, 30 min, 9%, 20%): ^{1}H NMR 5.22 (s, 2H), 6.73 (s, 1H), 7.67 (t, 2H), 7.75 (t, 1H), 8.38 (d, 2H); ^{13}C NMR 53.19 (1C), 59.85 (1C), 61.30 (1C), 128.51 (2C), 129.16 (2C), 133.98 (1C), 136.87 (2C),

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[72] The experimental procedure used for monoalkylation of C_{70} was similar to that used for C_{60}

[73] Chen prepared **3g** by reaction of C_{60} dianion with benzyl bromide. See ref 52.

136.89 (1C), 137.35 (2C), 140.29 (2C), 140.35 (2C), 141.73 (2C), 141.74 (2C), 141.87 (2C), 142.03 (2C), 142.21 (2C), 142.24 (2C), 142.63 (2C), 142.71 (2C), 143.37 (2C), 144.64 (2C), 144.99 (2C), 145.45 (2C), 145.49 (2C), 145.52 (2C), 145.69 (2C), 145.81 (2C), 146.02 (2C), 146.26 (2C), 146.27 (2C), 146.44 (2C), 146.50 (2C), 147.23 (2C), 147.34 (1C), 147.62 (1C), 153.84 (2C), 154.72 (2C), 195.97 (1C); MS 720.3 (100), 840.2 (60) (M$^-$); UV−vis 307.7, 324.3, 434.5.

3,3-Dimethyl-1-([60]fulleren-1(2*H*)-yl)-2-butanone (3i) (50 °C, 50 min, 19%, 27%): ^{1}H NMR 1.58 (s,9H), 4.72 (s,2H), 6.52 (s,1H); ^{13}C NMR 26.91 (3C), 44.69 (1C), 51.50 (1C), 59.91 (1C), 61.18 (1C), 136.86 (2C), 137.26 (2C), 140.27 (2C), 140.31 (2C), 141.70 (2C), 141.72 (2C), 141.86 (2C), 142.01 (2C), 142.18 (2C), 142.24 (2C), 142.62 (2C), 142.70 (2C), 143.37 (2C), 144.63 (2C), 144.98 (2C), 145.45 (2C), 145.48 (2C), 145.50 (2C), 145.64 (2C), 145.80 (2C), 146.01 (2C), 146.24 (2C), 146.27 (2C), 146.43 (2C), 146.49 (2C), 147.20 (2C), 147.34 (1C), 147.60 (1C), 153.78 (2C), 154.74 (2C), 212.12 (1C); MS 720.2 (100), 820.3 (50) (M$^-$); UV−vis 306.5, 327.9, 434.5.

Methyl 3-([60]fulleren-1(2*H*)-yl)crotonate (3j) (50 °C, 15 min, 6%, 10%): ^{1}H NMR 3.86 (s, 3H), 4.35 (q, 2H), 6.45 (s, 1H), 6.62 (qq, 1H), 7.90 (p, 1H); ^{13}C NMR 49.59 (1C), 51.90 (1C), 59.14 (1C), 63.93 (1C), 127.37 (1C), 136.59 (2C), 140.65 (4C), 142.02 (4C), 142.13 (2C), 142.29 (2C), 142.39 (2C), 142.48 (2C), 142.70 (4C), 142.92 (2C), 142.93 (2C), 143.57 (2C), 144.84 (2C), 145.03 (2C), 145.71 (2C), 145.76 (2C), 145.83 (2C), 145.98 (2C), 146.07 (1C), 146.10 (2C), 146.52 (2C), 146.58 (2C), 146.75 (4C), 147.11 (2C), 147.62 (1C), 147.80 (1C), 153.32 (2C), 154.44 (2C), 165.56 (1C); MS 720.2 (100), 820.2 (20) (M$^-$); UV−vis 306.5, 324.3, 433.2.

1-(*β*-Naphthylmethyl)-1,2-dihydro[60]fullerene (3k) (50 °C, 20 min, 9%, 18%): ^{1}H NMR 4.95 (s, 2H), 6.73 (s, 1H), 7.48−7.57 (m, 2H), 7.87−7.99 (m, 4H), 8.27 (s, 1H); ^{13}C NMR 53.78 (1C), 59.58 (1C), 66.26 (1C), 126.71 (1C), 126.90 (1C), 128.29 (1C), 128.33 (1C), 128.83 (1C), 129.44 (1C), 130.77 (1C), 133.17 (2C), 133.59 (2C), 133.78 (2C), 136.38 (2C), 136.62 (2C), 140.33 (2C), 140.55 (2C), 141.90 (2C), 141.96 (2C), 142.20 (2C), 142.27 (2C), 142.33 (2C), 142.48 (2C), 142.87 (4C), 143.53 (1C), 144.85 (2C), 145.00 (2C), 145.67 (2C), 145.69 (2C), 145.75 (2C), 145.83 (2C), 146.06 (2C), 146.46 (2C), 146.53 (3C), 146.67 (1C), 146.70 (2C), 147.21 (2C), 147.58 (1C), 147.73 (1C), 153.98 (2C), 155.42 (2C); MS 720.2 (100), 862.2 (30) (M$^-$); UV−vis 433.2.

Methyl ([70]fulleren-1(2*H*)-yl) acetate (5a) (50 °C, 1 h, 25%, 31%): ^{1}H NMR 3.91 (s, 2H), 3.98 (s, 3H), 4.70 (s, 1H); ^{13}C NMR (1,2-dichlorobenzene-d_4) 48.88 (1C), 52.04 (1C), 52.08 (1C), 53.04 (1C), 133.76 (2C), 133.79 (2C), 134.82 (6C), 137.76 (2C), 140.42 (2C), 141.44 (2C), 142.55 (2C), 142.88 (2C), 143.14 (2C), 144.71 (4C), 145.76 (2C), 146.44 (2C), 146.72 (2C), 147.01 (2C), 147.19 (4C), 147.58 (2C), 148.81 (2C), 148.87 (2C), 149.06 (2C), 149.27 (2C), 149.51 (2C), 149.60 (2C), 149.92 (2C), 150.67 (2C), 150.81 (2C), 151.16 (2C), 151.20 (2C), 151.22 (1C), 151.24 (1C), 155.14 (2C), 158.68 (2C), 170.05 (1C); MS 840.2 (100), 914.2 (90) (M$^-$); UV−vis 398.3, 462.3.

Methyl ([70]fulleren-5(6*H*)-yl) carboxylate (5b) (50 °C, 1 h, 3%, 4%): ^{1}H NMR 3.51 (q, 2H), 3.85 (s, 3H), 4.83 (s, 1H); ^{13}C NMR 47.94 (1C), 49.21 (1C), 51.35 (1C), 52.04 (1C), 131.57 (2C), 131.67 (1C), 131.77 (2C), 132.24 (1C), 132.47 (1C), 132.56 (1C), 132.69 (1C), 140.39 (1C), 140.91 (1C), 142.21 (1C), 142.48 (1C), 142.71 (1C), 142.85 (1C), 144.08 (1C), 144.17 (2C), 144.63 (1C), 144.72 (1C), 144.76 (1C), 144.82 (1C), 145.15 (1C), 145.24 (1C), 145.35 (1C), 145.38 (1C), 145.41 (2C), 145.47 (1C), 145.59 (2C), 146.14 (1C), 146.29 (1C), 146.52 (1C), 146.71 (1C), 146.84 (1C), 146.91 (1C), 147.12 (1C), 147.32 (2C), 147.37 (1C), 147.40 (1C), 147.56 (2C), 147.59 (1C), 147.90 (1C), 148.22 (1C), 148.30 (1C), 148.35 (1C), 148.38 (1C), 148.50 (1C), 149.15 (2C), 149.40 (1C), 149.43 (1C), 149.50 (1C), 149.62 (1C), 149.70 (1C), 150.31 (1C), 150.42 (1C), 150.47 (1C), 150.88 (1C), 150.93 (1C), 151.61 (1C), 151.85 (1C), 151.94 (1C), 152.59 (1C), 155.02 (1C), 169.96 (1C); MS 840.2 (100), 914.2 (70) (M$^-$); UV−vis 363.6, 397.1.

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Supporting Information Available: ^{1}H and ^{13}C NMR, HPLC, MS, and UV−vis spectra for compounds **3a**−**k** and **5a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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