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Alkylation of Dihydrofullerenes

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The fulleride dianions C_{60}^{2-} and C_{70}^{2-} were generated by deprotonation of the corresponding hydrogenated fullerenes, 1,2-$C_{60}H_2$ and 1,2-$C_{70}H_2$. These anions were prepared in the presence of a variety of alkylating agents, and mono- or dialkylated products were obtained. Alkylation was not successful with sulfonate ester alkylating agents. Deprotonation of monoalkylated compounds, followed by second alkylation with a different alkylating agent, produced heterodialkylated compounds. The monoalkyated material was invariably the 1,2-isomers, while the dialkylated materials were generally 1,4-isomers, although some 1,2-isomer was observed in the C_{70} context. The major product from alkylation of C_{70}^{2-} was the 7,23-isomer **13a**, a structure where the alkylation took place near the equator of the fullerene cage, rather than at the more strained carbons near the poles.

Introduction

One of the pillars of organic synthesis is the regiospecific deprotonation of carbon and subsequent alkylation of the resulting anions. The alkylation of fullerene anions presents the possibility of reversing the normal reactivity of a fullerene from electrophile to nucleophile. This reversal in reactivity could in principle provide an entrance to alkylated products with regiochemistry not directly obtainable by current methods. Currently, fullerene anions are most often provided by the reduction of fullerenes, but deprotonation of hydrogenated fullerenes is another potentially useful route. Different isomeric hydrogenated fullerenes offer the possibility of routes to different isomeric alkylated fullerene derivatives, something that is not possible through simple reduction followed by alkylation.

We have been investigating the synthesis and reactivity of hydrogenated fullerenes.[1−6] We and others have developed synthetic methods for the preparation of single isomers of $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$,[1,7−9] $C_{70}H_2$, $C_{70}H_4$, $C_{70}H_8$,[6] and $C_{70}H_{10}$,[5] additional $C_{70}H_n$ species,[10−12] as well as other, more highly hydrogenated fullerene species.[13,14]

These hydrogenated fullerenes offer a versatile entry point for further fullerene derivatization. Fullerene C−H bonds are quite acidic: the pK_a values of $C_{60}H_2$ are remarkably low for a hydrocarbon (pK_{a1} = 4.7, pK_{a2} = 16).[15] These data suggest that fullerene anions (fullerides) should be readily available by deprotonation of hydrogenated fullerenes. In principle, it should be possible to generate C_{60}^{6-} hexaanion by completely deprotonating $C_{60}H_6$ or to make any of a series of $C_{60}H_n^{m-}$ species by the appropriate choice of starting compound and then controlling the amount of base added. $C_{60}H_n^{m-}$ species differ from C_{60}^{m-} ions in that sp^3 centers are present, and these tetrahedral centers may lead to an increase in charge and in nucleophilicity at a limited set of carbon atoms. If this occurs, it would offer a degree of control over the range of regioisomers formed by alkylation.

Successful implementation of this deprotonation−alkylation strategy in fullerenes offers the possibility to selectively control the functionalization and synthetic elaboration of these molecules. The potential exists for

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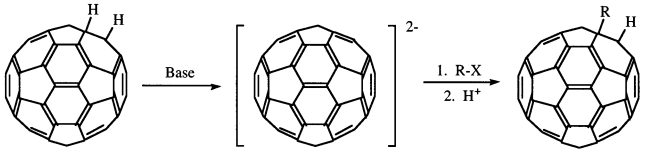
sequential deprotonation−alkylation steps in which the regiochemistry of the resulting alkylated species reflects the regiochemistry of the starting reduced fullerene. For example, if the starting regiochemistry can be manifest in the product, then regiochemically pure $R_1R_2R_3R_4R_5R_6C_{60}$ species could be made from 1,2,33,41,42,50-$C_{60}H_6$. Our first work toward this goal is reported here.

Preparation of fulleride anions by deprotonation of fullerene C−H bonds is a complementary route to formation of these anions by direct reduction of C_{60} or C_{70}. Solutions of fulleride anions have been produced traditionally by electrochemical or by dissolving-metal reduction of the parent fullerene.[16−20] Alternatively, reduction of C_{60} in THF solution with thiolates[21,22] or with quinone dianions can achieve the same goal[23] or by a number of different alkali metal reductions.[24−27] Alkylation of fullerene ions prepared electrochemically[28−30] and by dissolving-metal reduction has been achieved, although a mixture of products was obtained.[31] Alkylation of fullerene anions produced by quinone dianion and by thiolates has been successful as well.[22,23]

Results and Discussion

Monoalkylation. Given the acidity of hydrogenated fullerenes, double deprotonation of 1,2-$C_{60}H_2$ (**1**) [1,10,32−35] to produce C_{60}^{2-} should be possible with very mild bases. Treatment of the resulting dianion with suitable alkylating agents should then provide the desired mono- and/or dialkyl fullerenes (Scheme 1).

SCHEME 1



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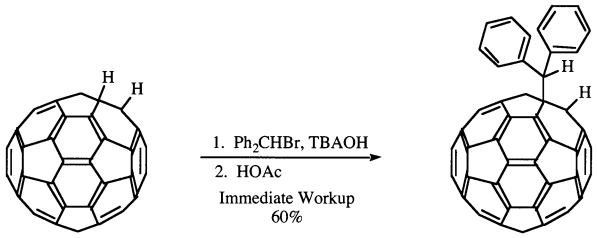
SCHEME 2



1 **2**

Treatment of **1** with base (BuLi, LiHMDS, NaH, DBU, K_2CO_3, or KOtBu) in THF, toluene, benzene, methanol−THF, or *o*-dichlorobenzene solution containing a significant excess of benzyl bromide produced little if any mono- or dialkyl fullerene. The majority of the fullerene-derived product was an uncharacterized brown material that was insoluble in toluene but soluble in THF.

A survey of additional common bases did not provide a solution to this problem. However, we found that the C_{60}^{2-} dianion can be generated in benzonitrile solution by treating **1** with tetrabutylammonium hydroxide. The characteristic deep red color of the dianion forms very rapidly, but in the presence of excess diphenylmethyl bromide, the dark red color is rapidly replaced by a deep green color, typical of an RC_{60} anion. Immediately quenching the reaction mixture with acetic acid produces a mixture of $Ph_2CHC_{60}H$ (**2**) and C_{60} (Scheme 2). No unreacted **1** was detected under these conditions.

HPLC purification of this crude reaction mixture on a Cosmosil Buckyprep column (100% toluene mobile phase) provided clean samples of **2** in 60% yield. The absorption spectrum of **2** is virtually superimposable on the spectrum of **1** (Figure 1), indicating that the two sp^3 carbons of **2** are arranged in a 1,2 fashion, an addition pattern common among fullerene derivatives.

Scrupulous deoxygenation is required for successful alkylation. The best yields (typically 60% isolated yield) were obtained in reactions where freeze−pump−thaw (FPT) deoxygenation was used to remove oxygen from the reaction mixture. Even under these conditions, roughly 30% yields (by HPLC) of C_{60} were obtained in every example. This undesired oxidation could not be suppressed, even with FPT deoxygenation of the reaction mixture and the base solution and carrying out the reaction in an inert-atmosphere glovebox.

Deoxygenation of the base solution by FTP did not result in better yields than did deoxygenation by simple sparging. Since increasingly stringent deoxygenation methods do not affect the amount of C_{60} formed, we believe that the roughly 30% of the C_{60}^{2-} dianion is lost

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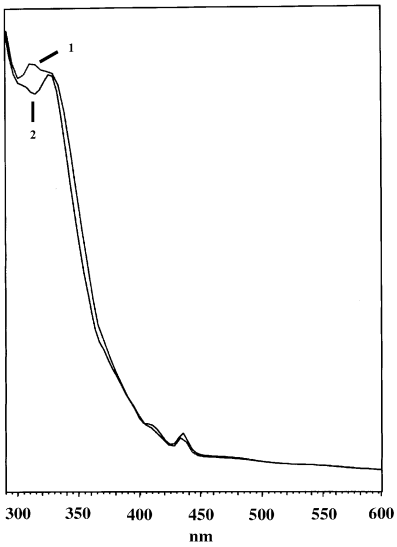
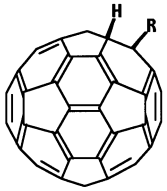


FIGURE 1. Absorption spectra of **2** and 1,2-$C_{60}H_2$.

to oxidation through electron transfer to the alkyl halide,[36] followed by radical reactions that do not lead to alkylated fullerenes. We have attempted to detect 1,2-diphenylethane from the alkylation of $C_{60}H_2$ with benzyl bromide, but were not able to do so definitively.

Using the same conditions for alkylation of **1** with Ph_2-CHBr, we have been able to monoalkylate $C_{60}H_2$ with several other alkyl halides. However, not all alkyl halides will alkylate the C_{60}^{2-} anion. Specifically, alkylation was achieved with Ph_2CHBr (**2**, 60%), propargyl bromide (**3**, 21%), allyl bromide (**4**, 54%), and $PhCH_2Br$ (**5**, 38% by

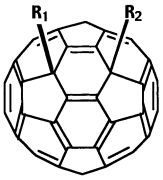


R = $CHPh_2$ (**2**), CH_2CCH (**3**), $CH_2CH{=}CH_2$ (**4**), CH_2Ph (**5**)

HPLC). In the latter case, dialkylation was very rapid (see below) and made isolation of **5** very difficult. No alkylation was detected when octyl bromide, octyl iodide, or cyclopropylmethyl bromide was used. All attempts to alkylate C_{60}^{2-} with sulfonate esters were unsuccessful. These results are consistent with a radical mechanism.[23]

Homodialkylation. If these reactions were allowed to proceed for several hours, dialkylated products were isolated. For example, stirring a deoxygenated mixture of **1**, TBAOH, and excess benzyl bromide produced a 45% isolated yield of **6**. Dibenzylation of C_{60}^{2-} generated by *p*-benzoquinone dianion reduction of C_{60} is known to produce 1,4-disubstitution.[23] The 1,4-regiochemistry is established by comparison with literature spectra.[37] In addition, we have successfully produced 1,4-dialkylated derivative **7** in 49% yield, using allyl bromide. Interestingly, reaction with $PhCH_2Br$, the second alkylation step (producing **6**), occurred so rapidly that dialkyl products dominated the reaction mixture within minutes of the addition of base.

Heterodialkylation. Much of the potential of the deprotonation−alkylation route to fullerene derivatives lies in the ability to sequentially replace several protons with different alkyl groups. To explore this possibility, we treated **2** with TBAOH in THF solution containing excess MeOTs, leading to a deep green solution characteristic of the RC_{60}^- anion, but after 24 h there was no detectable formation of $CH_3C_{60}(CHPh_2)$. The anion slowly decomposed to a brownish material that was nearly insoluble in toluene. These results are consistent with our experience attempting to alkylate C_{60}^{2-} with sulfonate esters. However, treatment of **2** in PhCN solution with TBAOH and allyl bromide produces $CH_2{=}CHCH_2C_{60}$-$(CHPh_2)$ (**8**). The UV−vis spectrum of this compound is that of a 1,4-dialkylated product, and the ^1H NMR and ^{13}C NMR are consistent with the expected heterodialkylated product. Similarly, we have successfully produced the heterodialkylation product with benzyl bromide as the alkylating agent, producing 1,4-$PhCH_2C_{60}(CHPh_2)$ (**9**). 1,2-Dialkylated products were not observed in these reactions.



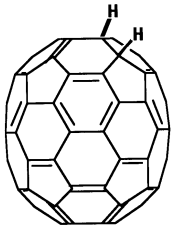
$R_1 = R_2 = CH_2Ph$ **6**

$R_1 = R_2 = CH_2CH{=}CH_2$ **7**

$R_1 = CHPh_2$, $R_2 = CH_2CH{=}CH_2$ **8**

$R_1 = CHPh_2$, $R_2 = CH_2Ph$ **9**

Alkylation of C_{70} Anions Derived from 1,2-$C_{70}H_2$. The alkylation of C_{70} anions derived from 1,2-$C_{70}H_2$ (**10**), as well as other $C_{70}H_n$ species, poses an interesting regiochemical question. In C_{70}^{2-} the charge is delocalized over five symmetrically unique positions,[38] any one of which may react in the first alkylation step.



10

In practice, deprotonation of **10** (prepared by Zn(Cu) reduction of C_{70}[6]) in the presence of benzyl bromide, leads to similar color changes as seen with **1**, although complete alkylation requires significantly more reaction time than in the C_{60} case.

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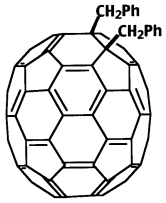
HPLC analysis of the crude reaction mixture reveals a set of three bands containing dialkylated products (by mass spectrometry). The first and third bands contained single compounds **13** (10% isolated yield) and **12** (1% isolated yield), while the middle band contained several species.

The middle band resolved into two fractions upon passage through a Cosmosil Buckyprep column (100% toluene mobile phase). Examination of the ^{1}H NMR spectrum of the first fraction (10% isolated yield) revealed an AB pattern and a singlet in the benzyl methylene region. The ^{13}C NMR spectrum showed two fullerene sp^3 resonances, two benzylic resonances, and more than 60 sp^2 resonances. This combination of data indicates that this band is a mixture of two compounds, both of which have significant symmetry. We were unable to resolve this fraction into its individual components.

The second fraction of the middle band was composed of **11**. The ^{1}H NMR spectrum of **11** consisted of two singlets for the benzyl methylene resonances, indicating two inequivalent benzyl groups. The absence of an AB pattern suggests that the two benzyl groups are on a plane of symmetry. The ^{13}C NMR spectrum showed two fullerene sp^3 resonances and 31 fullerene sp^3 resonances, several of which having double intensity (indicative of overlapping resonances). These data are consistent with a plane of symmetry containing two different benzyl groups. In addition, the absorption spectrum of this compound is very similar to that of **10** (see Figure 2). These data suggest that the structure of this minor isomer (1% yield) is 1,2-$(PhCH_2)_2C_{70}$ (**11**). While this is a sterically crowded arrangement, 1,2-$(PhCH_2)_2C_{60}$ has been previously prepared in low yield.[37]



11

The ^{1}H NMR spectrum of **12** exhibited a single AB pattern for the benzyl methylene protons. The ^{13}C NMR spectrum possessed one fullerene sp^3 resonance, one benzylic resonance, four phenyl resonances, and at least 32 fullerene sp^2 resonances (some overlapping). These data suggest that **12** has either a plane of symmetry or a C_2 axis of symmetry. The limited amount of material available made it impossible to definitively assign the structure of this minor product.

Examination of the ^{1}H NMR spectrum of the first fraction, containing **13**, revealed a single AB pattern for the benzyl methylene resonances, indicating a structure with either a plane of symmetry or a C_2 axis of symmetry and hindered rotation of the benzyl groups. The ^{13}C NMR spectrum exhibited a single benzyl resonance and a single fullerene sp^3 resonance. The sp^2 region included four resonances from the phenyl CH carbons (three with NOEs from attached hydrogens) and 34 single intensity fullerene resonances. This confirms the C_2 symmetry of this isomer.

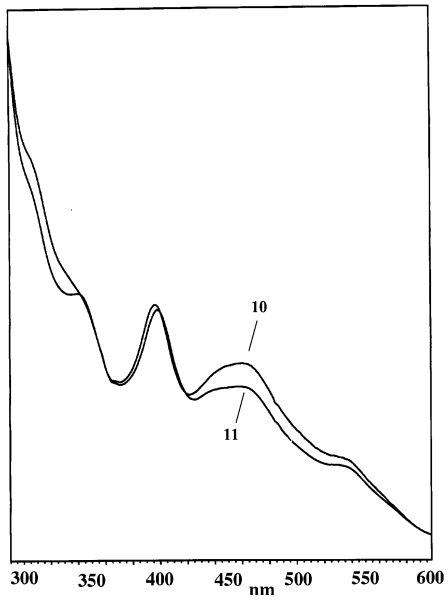
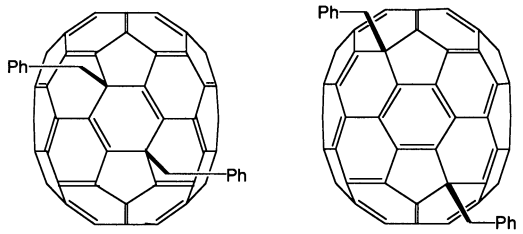


FIGURE 2. Comparison of absorption spectra of two different 1,2-$C_{70}R_2$ species: **10** and **11**.

A number of structures with C_2-symmetry are possible. Two representative examples are shown below. Structure **13a** was proposed earlier for the Bn_2C_{70} species prepared by alkylation[39] of electrochemically generated C_{70}^{2-}. This



13a **13b**

assignment was based, in turn, on calculations by Cahill on the thermodynamically most stable isomers of $C_{70}H_2$ with nonadjacent hydrogens.[40] Given the fact that this reaction is probably kinetically controlled rather than thermodynamically controlled, we used ^{13}C INADEQUATE NMR methods to definitively answer this structural question.

A sample of 13% ^{13}C-enriched **10** was prepared, purified, and subjected to alkylation with $PhCH_2Br$. INADEQUATE NMR experiments revealed 46 of 52 expected correlations. The connectivity exposed by these correlations allowed us to make a definitive structural assignment. The key observation from the INADEQUATE spectrum is that there are two sp^2 carbons that are correlated (adjacent) to each other, and both are correlated to the sp^3 carbon (Figure 3). Only one C_2 structure meets these requirements: **13a**. The connectivity revealed by the rest of the correlations is also consistent with this structure.

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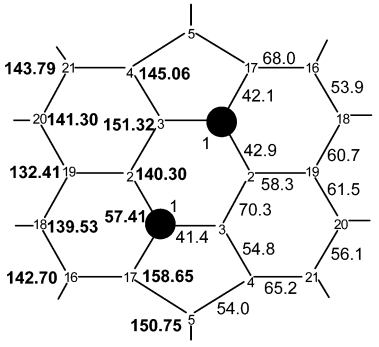

FIGURE 3. A portion of the structure of **13a** as determined by INADEQUATE NMR spectroscopy. Numbers in bold on the left side are chemical shifts, numbers in plain font on the right are $^{13}C-^{13}C$ coupling constants, and the numbers on the vertexes denote equivalent carbons.

The preference for alkylation of C_{70}^{2-} near the equator indicates high reactivity in carbons that are typically the least reactive in the neutral fullerene. While the charge is significantly delocalized in C_{70}^{2-}, AM1 calculations[41] of the SOMO (which is likely to be involved in the irreversible, C−C bond forming step) suggest that this key orbital has the highest density at the very positions (C7/C23, which are equivalent by symmetry) where we find the benzyl groups attached. After the first alkylation step occurs at C7, the resulting $PhCH_2C_{70}^-$ species shows significant charge concentration at C23, the other carbon to which we find benzyls attached. In contrast to the situation found for RC_{60}^- anions, the charge density is not as high at the carbons adjacent to the alkylated carbon.

Conclusions

We have demonstrated that it is possible to use reduced fullerenes as precursors to fulleride anions under synthetically useful conditions. Yields for monoalkylation are typically near 60% with some loss of dianion to oxidation to the parent fullerene. Alkyl halides that can easily produce radicals upon electron transfer are the only halides that are useful in this reaction. Aliphatic chlorides and all sulfonates tested do not react with C_{60}^{2-} produced under these conditions. A second alkylation step does occur within a few minutes to a few hours of reaction time. Both the first and the second alkylation steps appear to be much more efficient with alkyl halides than with alkyl sulfonates. $C_{70}H_2$ was deprotonated and alkylated under similar conditions, and while a mixture of products was obtained, it appears that the most nucleophilic site is C7. The resulting anion ($PhCH_2C_{70}^-$) alkylates at C23, producing a 1,4-dialkylated compound whose structure was assigned by ^{13}C INADEQUATE experiments. Rather than addition to the strained carbons at the poles of the molecule, addition occurs to positions near the equator, offering a route to novel C_{70} derivatives.

Experimental Section

General experimental details are available in previous publications.[1] Representative procedures for the preparation of mono- and dialkylfullerenes are given below. All reactions were carried out under Ar or N_2 atmospheres using standard needlestock techniques. Unless otherwise noted, yields refer to isolated, HPLC-purified material.

General Procedure for Alkylation of Dihydrofullerenes: 1-Diphenylmethyl-1,2-dihydro[60]fullerene (2). $C_{60}H_2$ (63.4 mg, 0.088 mmol), diphenylmethyl bromide (2.36 g, 9.57 mmol), and PhCN (31 mL) were combined in a 100 mL Schlenk flask. This mixture was subjected to 10 freeze−pump−thaw (FPT) cycles. The solution was warmed to room temperature and put under an Ar atmosphere. 3 mL of TBAOH (1 M in MeOH, deoxygenated by sparging with Ar) was quickly added and the reaction mixture turned deep red then quickly turned deep green. The reaction was quenched immediately with 2 mL of acetic acid, resulting in a brown solution. This solution was filtered and passed through a short silica plug to remove tetrabutylammonium salts. The PhCN was removed by short-path vacuum distillation. The resulting brown solid was dissolved in CS_2 and passed through another silica plug to remove the diphenylmethyl bromide starting material. This solution was diluted with toluene and concentrated in vacuo. The product was purified by HPLC (Cosmosil semipreparative Buckyprep column, toluene mobile phase, 5 mL/min flow rate, monitored at 400 nm), producing 46.6 mg (0.052 mmol, 60% yield): MS (negative ion FABS) *m/z* 888; ^1H NMR (200 MHz, CS_2/acetone-d_6) δ = 6.04 (s, 1 H), 6.78 (s, 1 H), 7.37 (m, 2 H), 7.49 (m, 4 H), 8.08 (m, 4 H); ^{13}C NMR (100 MHz, CS_2/acetone-d_6) δ = 60.25, 66.81, 70.68, 128.31, 129.47, 131.07, 136.75, 136.9, 139.55, 140.66, 140.76, 141.97, 142.05, 142.19, 142.51, 142.57, 142.63, 143.03, 143.08, 143.69, 144.96, 145.21, 145.82, 145.83, 145.97, 146.25, 146.58, 146.70, 146.85, 147.38, 147.65, 147.87, 155.00, 155.13.

1-Propargyl-1,2-dihydro[60]fullerene (3): MS (positive ion MALDI-MS), *m/z* 760; ^1H NMR (200 MHz, CS_2/acetone) δ = 2.86 (t, 1H), 4.41 (d, 2H), 6.81 (s, 1H); ^{13}C NMR (75 MHz, CS_2/acetone) δ = 40.50, 62.73, 66.98, 77.74, 83.34, 139.95, 139.97, 143.47, 143.60, 145.03, 145.10, 145.38, 145.50, 145.71, 145.90, 145.94, 146.57, 147.93, 148.01, 148.69, 148.75, 148.80, 149.10, 149.19, 149.50, 149.58, 149.70, 149.78, 150.42, 150.60, 150.80, 157.31, 157.66; HR MALDI (9-nitroanthracene matrix) 760.027, calcd for $C_{63}H_4$ 760.031.

1-Allyl-1,2-dihydro[60]fullerene (4): MS (negative ion FABS-MS), *m/z* 762; ^1H NMR (200 MHz, CS_2/benzene) δ = 3.99 (d, 2h), 5.67 (m, 2H), 6.33 (s, 1H), 6.68 (m, 1H); ^{13}C NMR (100 MHz, CS_2/benzene) δ = 51.36, 58.90, 64.55, 121.84, 133.64, 136.40, 136.64, 140.56, 140.59, 141.96, 142.23, 142.27, 142.34, 142.51, 142.89, 143.57, 144.88, 145.02, 145.68, 145.70, 145.77, 145.85, 146.08, 146.41, 146.49, 146.54, 146.70, 146.72, 147.27, 147.58, 147.73, 154.03, 155.61.

1-Benzyl-1,2-dihydro[60]fullerene (5): MS (negative ion FABS-MS), *m/z* 812; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ = 4.76 (s, 2H), 6.62 (s, 1H), 7.41 (m, 1H), 7.50 (m, 2H), 7.90 (m, 2H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ = 52.50, 59.09, 66.0, 127.80, 127.72, 128.75, 131.50, 132.05, 135.80, 135.95, 136.25, 139.90, 140.05, 141.50, 142.62, 141.81, 141.66, 141.92, 142.18, 142.40, 143.13, 144.42, 144.60, 145.33, 145.40, 145.81, 146.05, 146.08, 146.20, 146.95, 147.20, 153.90, 155.30.

General Procedure for Homodialkylation of Dihydrofullerenes: 1,4-Dibenzyl-1,4-dihydro[60]fullerene (6). $C_{60}H_2$ (**1**) (50.1 mg, 0.069 mmol), benzyl bromide (1.0 mL, 4.07 mmol), and 25 mL of PhCN were combined in a 100 mL Schlenk flask. The mixture was subjected to 10 FPT cycles, warmed to room temperature, and put under an Ar atmosphere. Then 3.5 mL of TBAOH (1M in MeOH, sparged with Ar) was quickly added and the reaction mixture turned deep red and immediately deep green. The reaction was allowed to stir for 2 h and slowly turned to a brown solution. HCl (10%, 2 mL) was added, and the PhCN was removed using a short-path vacuum distillation. The resulting brown solid was dissolved in toluene and washed with 10% HCl. The product was purified by HPLC [Cosmosil semipreparative Buckyprep column, toluene/hexane (70:30) mobile phase, 5 mL/min flow rate, and monitored at 400 nm], producing 28.1 mg (0.0311 mmol, 45%): MS (negative ion FABS), *m/z* 903 (MH); ^1H NMR (200 MHz, $CDCl_3$) δ = 3.74

(41) The SOMO was calculated using MacSpartan Pro, Wavefunction, Inc.

(q_{AB}, 4H), 7.34 (m, 2H), 7.46 (m, 4H), 7.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 48.42, 50.32, 127.38, 128.24, 130.93, 136.09, 137.60, 138.58, 140.31, 141.79, 141.81, 142.27, 142.34, 142.44, 142.77, 142.89, 142.98, 143.52, 143.73, 143.92, 144.04, 144.08, 144.16, 144.47, 144.52, 144.58, 144.80, 145.29, 145.97, 146.69, 146.71, 146.77, 146.98, 148.43, 151.51, 157.74; HR MALDI (9-nitroanthracene matrix) 902.103, calcd for $C_{74}H1_4$ 902.110.

1,4-Diallyl-1,4-dihydro[60]fullerene (7): MS (negative ion FABS-MS), *m/z* 802; ^{1}H NMR (200 MHz, CS_2/acetone) δ = 3.90 (m, 4H), 5.61 (m, 4H), 6.68 (m, 2H); ^{13}C NMR (100 MHz, CS_2/acetone) δ = 47.82, 59.75, 120.94, 133.83, 139.02, 139.63, 141.39, 142.67, 142.73, 143.16, 143.25, 143.33, 143.65, 143.83, 144.44, 144.62, 144.78, 144.93, 144.98, 145.08, 145.44, 145.55, 145.80, 146.13, 146.69, 147.54, 147.59, 147.85, 148.06, 149.25, 149.38, 152.26, 158.12.

General Procedure for Heterodialkylation of Dihydrofullerenes: (Diphenylmethyl)(allyl)-1,4-dihydro[60]fullerene (8). $HC_{60}(CHPh_2)$ (46.6 mg, 0.053 mmol), allyl bromide (3 mL), and PhCN (23 mL) were combined in a 100 mL Schlenk flask. This mixture was subjected to 10 freeze−pump−thaw (FPT) cycles. The solution was warmed to room temperature and put under an Ar atmosphere. Then 4.5 mL of TBAOH (1M in MeOH, sparged with Ar) was quickly added and the reaction mixture turned deep green and slowly became brown. The reaction was stirred overnight and quenched with 4.5 mL of AcOH. This solution was filtered and passed through a short silica plug to remove tetrabutylammonium salts. The PhCN was removed by short-path vacuum distillation. This solution was diluted with toluene and concentrated in vacuo. The product was purified by HPLC [Cosmosil semipreparative Buckyprep column, toluene/hexane (70:30) mobile phase, 5 mL/min flow rate, monitored at 400 nm], producing 14.2 mg (0.015 mmol, 29% yield): MS (negative ion FABS-MS), *m/z* 929; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.84 (m, 2H), 5.40 (m, 2H), 5.56 (s, 1H), 6.42 (m, 1H), 7.42 (m, 6H), 7.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 59.08, 60.52, 64.49, 65.50, 119.91, 127.71, 127.74, 128.76, 128.77, 130.15, 130.27, 133.23, 134.39, 137.88, 138.70, 138.81, 138.95, 139.92, 139.97, 140.38, 141.39, 141.94, 141.97, 142.21, 142.37, 142.52, 142.56, 142.76, 142.94, 143.05, 143.10, 143.11, 143.15, 143.34, 143.46, 143.70, 143.75, 143.97, 143.99, 144.09, 144.10, 144.19, 144.22, 144.26, 144.33, 144.47, 144.55, 144.58, 144.61, 144.63, 144.88, 144.92, 145.04, 145.42, 145.60, 146.77, 146.84, 146.86, 147.06, 147.07, 147.30, 147.59, 148.44, 148.47, 148.58, 148.72, 151.24, 151.55, 156.48, 157.35.

(Diphenylmethyl)(benzyl)-1,4-dihydro[60]fullerene (9): 54% isolated yield; MS (negative ion FABS-MS), *m/z* 978; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.43 (q_{AB}, 2H), 5.48 (s, 1H), 7.20−7.55 (m, 14H, some residual solvent present), 7.98 (d, 2H), 8.05 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 47.97, 59.94, 64.15, 65.34, 127.05, 127.64, 127.68, 128.02, 128.49, 128.68, 130.00, 130.14, 130.64, 135.46, 137.74, 138.49, 138.60, 138.67, 139.65, 140.20, 141.28, 141.61, 141.75, 142.03, 142.10, 142.33, 142.39, 142.63, 142.70, 142.88, 142.94, 142.96, 143.09, 143.34, 143.53, 143.74, 143.88, 143.93, 143.95, 143.98, 144.06, 144.15, 144.22, 144.35, 144.69, 144.76, 144.79, 145.25, 145.35, 146.58, 146.63, 146.66, 146.70, 146.84, 146.86, 147.29, 147.30, 148.26, 148.37, 148.46, 151.11, 151.40, 156.20, 156.72.

Dibenzyldihydro[70]fullerenes. ^{13}C-enriched $C_{70}H_2$ (59.1 mg, 0.07 mmol, prepared from ca. 13% ^{13}C C_{70}), benzyl bromide (250 μL, 2 mmol), and benzonitrile (60 mL) were combined in a 250 mL Schlenk flask and deoxygenated through 10−12 FPT cycles. TBAOH (1 M in methanol), present in a separate 25 mL Schlenk flask, was also deoxygenated by 15 FPT cycles. After degassing, the two flasks were placed under an Ar atmosphere, and 500 μL (1.6 mmol) of TBAOH in MeOH (sparged with Ar) was then added to the reaction mixture using a gastight syringe. The solution turned a darker brown immediately and stirred for 18 h. At 18 h, 1 mL of acetic acid was added for workup. Ammonium salts were removed by passing the solution through a silica plug and eluting with toluene. The toluene was then removed in vacuo to minimize solution quantity. Short-path vacuum distillation was then used to remove the benzonitrile. The resulting brown solid was dissolved in toluene and concentrated. This solution was then purified by two different HPLC columns: first by preparative HPLC [4.6 × 250 mm Cosmosil 5PBB column, toluene:hexane (70:30) as mobile phase, monitored at 310 nm] to obtain three fractions. Fraction 1 contained **13a** and fraction 3 contained the minor product **12**. Fraction 2 was further purified by preparative HPLC (4.6 × 250 mm Buckyprep column, toluene as mobile phase, monitored at 310 nm) and was resolved into two chromatographic bands. The first band was determined to be an inseparable mixture of two isomers, and the second band was composed of a single compound (**11**). The yield of the four resolved components (**13a**, **11**, and **12**) was 10%:1%:1%, with an additional 10% yield of the unresolved pair of isomers.

1,2-Dibenzyldihydro[70]fullerene (11): MS (negative ion FABS-MS, ca. 13% ^{13}C-enriched), *m/z* 1032; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ = 4.15 (s, 2H), 4.34 (s, 2H), 7.10−7.64 (m, 10H); ^{13}C NMR (150 MHz, CS_2/$CDCl_3$) δ = 60.22, 60.97, 130.85, 130.89, 130.93, 131.69, 133.54, 135.81, 139.03, 139.58, 142.63, 145.48, 145.86, 145.95, 146.00, 146.52, 146.59, 146.64, 147.13, 148.38, 148.48, 148.61, 148.85, 148.93, 149.26, 149.40, 149.48, 149.95, 150.28, 150.92, 151.02, 154.50, 159.99.

Dibenzyldihydro[70]fullerene (12): MS (negative ion FABS-MS, ca. 13% ^{13}C-enriched), *m/z* 1033; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.04 (q_{AB}, 4H), 7.15−7.45 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 46.29, 57.83, 127.44, 128.03, 128.32, 130.54, 130.77, 131.89, 132.50, 132.85, 134.06, 136.26, 138.81, 140.16, 141.63, 143.91, 144.13, 144.41, 145.05, 145.39, 145.61, 145.77, 146.72, 146.88, 148.29, 148.61, 148.73, 148.94, 149.45, 149.74, 150.02, 150.21, 150.54, 151.54, 152.30, 157.02, 158.21.

7,23-Dibenzyldihydro[70]fullerene (13a): MS (MALDI-MS), *m/z* 1033; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.66 (q_{AB}, 4H), 7.13−7.37 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 49.81, 57.43, 127.52, 128.29, 130.63, 132.24, 133.69, 134.11, 134.22, 135.78, 139.35, 140.12, 141.11, 142.06, 142.50, 142.82, 143.61, 144.33, 144.58, 144.87, 145.21, 145.30, 145.38, 145.91, 146.11, 146.88, 146.99, 147.09, 147.34, 147.44, 148.28, 148.48, 148.65, 148.76, 148.91, 149.71, 150.53, 150.63, 151.18, 158.50.

INADEQUATE NMR Experiments. Two ^{13}C INADEQUATE experiments were performed. Both were performed on Varian Inova spectrometers at 10 °C, one was performed at 100 MHz (exp1) and a second at 150 MHz (exp 2). Experiment 1 (exp 1) used a spectral width of 11 056 Hz and 16 384 real points in ω_2, and experiment 2 (exp 2) used a spectral width of 5422 Hz and 16 384 real points in ω_2. Digital oversampling by a factor of 36 (for exp 1) and 68 (for exp 2) was employed to reduce baseline distortions associated with the spectrometer's low-pass filters.[42] All experiments were recorded using the hypercomplex method of phase incrementation to obtain quadrature phase detection in ω_1.[43] The spectral width of ω_1 was the same as in ω_2, which led to folding of the spectrum, and 1024 (for exp 1) and 2048 (for exp 2) complex points were collected, and the total number of transients recorded were 16 and 32 (for exp 1) and 8 and 16 (for exp 2) for real and complex data, respectively. For all experiments, the value of Δ for the double quantum polarization transfer was set to 4.3 ms, corresponding to a maximum magnetization transfer for $^1J_{CC}$ = 57 Hz that was the average of the sp^2−sp^2 one bond coupling constants. Decoupling of ^{1}H during the entire experiment was performed using the WALTZ scheme built into the spectrometer hardware. The total recycle delay (acquisition time plus relaxation delay) was set to 12.7 s (for exp 1) and 12.6 (for exp 2), which are approximately 0.64 (for exp 1) and 0.63 (for exp 2) multiplied by an average sp^2 ^{13}C spin−lattice relaxation time of 20 s (measured in $C_{60}H_2$).

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The ^{13}C T_1 relaxation times were measured by recording 11 1D experiments with relaxation delays T of 0.1, 0.5, 1, 2, 3, 4, 6, 11, 18, 28, and 45 s with proton decoupling. Intensities of the resonance peaks in the NMR spectra were determined as peak heights. The relaxation rate constants were obtained from nonlinear fits to $I(T) = I_\infty - (I_\infty - I_0)\exp(-R_1T)$, in which $I(T)$ is the intensity at time T, I_∞ is the intensity at time = infinity, and I_0 is the intensity at time = zero.

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Supporting Information Available: Characterization data (HPLC and ^{13}C NMR spectra) for **2**−**9** and **11**, absorption spectrum, and a figure showing the complete chemical shift assignments and J_{CC} values from the INADEQUATE experiments on **13a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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