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Single Electron Transfer-Promoted Photochemical Reactions of Secondary *N*-Trimethylsilylmethyl-*N*-benzylamines Leading to Aminomethylation of Fullerene C_{60}

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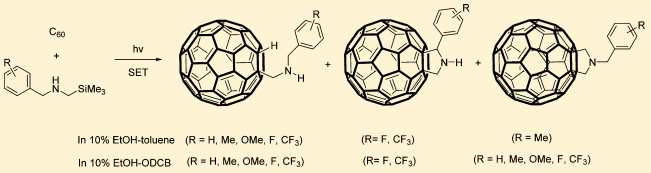
Supporting Information

ABSTRACT: Photoreactions between C_{60} and secondary *N*-trimethylsilylmethyl-*N*-benzylamines were explored to evaluate the feasibility of a new method for secondary aminomethylation of electron acceptors. The results show that photoreactions of C_{60} with these secondary amines in 10% EtOH-toluene occur to form aminomethyl-1,2-dihydrofullerenes predominantly through a pathway involving single electron transfer (SET)-promoted formation of secondary aminium radicals followed by preferential loss of the α-trimethylsilyl group. The aminomethyl radicals formed in this manner then couple with C_{60} or $C_{60}^{\bullet-}$ to form radical or anion precursors of the aminomethyl-1,2-dihydrofullerenes. In contrast to thermal and photochemical strategies developed previously, the new SET photochemical approach using α-trimethylsilyl-substituted secondary amines is both mild and efficient, and as a result, it should be useful in broadening the library of substituted fullerenes. Moreover, the results should have an impact on the design of SET-promoted C−C bond forming reactions. Specifically, introduction of an α-trimethylsilyl group leads to a change in the chemoselectivity of SET-promoted reactions of secondary amines with acceptors that typically favor aminium radical N−H deprotonation, leading to N−C bond formation. Finally, symmetric and unsymmetric fulleropyrrolidines are also generated in yields that are highly dependent on the electronic properties of arene ring substituents in amines, irradiation time, and solvent.

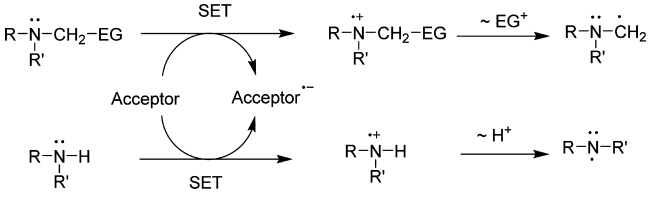


INTRODUCTION

Since the time that protocols were developed for their large-scale synthesis,[1] fullerenes have attracted the interest of chemists whose studies focus on utilizing chemical modifications to tune photochemical/photophysical properties and to introduce new functionality into these unique substances. These efforts have led to methods that enable the synthesis of fullerene derivatives that can be widely employed in the material[2−10] and biological[11−19] sciences. Among the large variety of synthetic methodologies devised thus far, photoinduced single electron transfer (SET) reactions with electron donors have become attractive for the preparation of substituted fullerenes because they can be carried out under environmentally benign conditions using visible light and they generate unique products.[20−25]

Owing to their modestly low oxidation potentials,[26] amines participate in a wide variety of photoinduced SET processes.[27−31] In these reactions, amines serve as electron donors to excited states of electron acceptors in processes that produce the respective amine radical cations (aminium radicals) and acceptor radical anions. In most typical reactions, aminium radicals derived from tertiary amines undergo loss of the electrofugal groups (e.g., deprotonation and decarboxylation)[27−37] to form carbon-centered aminomethyl radicals (Scheme 1), which then participate in C−C bond forming reactions with the acceptor anion radicals or their protonated counterparts. The results of a number of earlier studies demonstrated that aminium radicals, arising by SET oxidation of tertiary amines possessing α-trialkylsilyl substituents, undergo rapid[35] silophile-induced desilylation to generate amino-

Scheme 1



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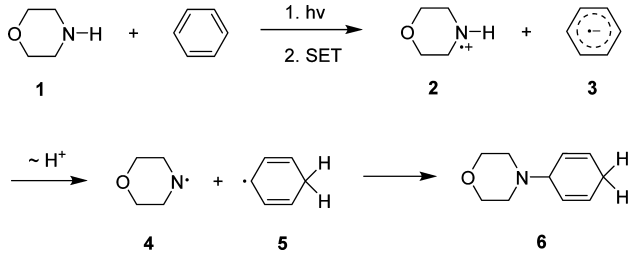
methyl radicals in a regioselective manner.[35,38] Moreover, the presence of α-trialkylsilyl groups in these amines reduces their oxidation potentials[39,40] and, consequently, extends the range of electron acceptors that can be utilized in these SET-promoted C−C bond forming processes. These properties have enabled the use of tertiary α-trialkylsilyl-substituted amines in a wide variety of SET-promoted photochemical reactions with saturated[41,42] and α,β-unsaturated ketones,[43,44] phthalimides,[45−47] and fullerene.[24b,25]

Primary and secondary amines also act as efficient electron donors to singlet and triplet excited states of ketones, olefins, and arenes.[41,48,49] However, in contrast to those formed from tertiary amines, primary and secondary aminium radicals typically undergo rapid N−H deprotonation to produce nitrogen-centered aminyl radicals (Scheme 1) or direct addition to acceptors. These processes, which often takes place more rapidly than α-CH deprotonation, serve as key steps in pathways leading to N−C bond-forming amination reactions. Examples of this behavior are seen in processes studied by Lattes[50] and Schmid.[51] Another is found in early studies by Bryce-Smith and co-workers,[48d] which show that secondary amines photoadd to benzene to generate 1,2- and 1,4-amination products. Specifically, photoreaction of morpholine (**1**) with benzene proceeds through the intermediacy of radical ions **2** and **3** and radicals **4** and **5** to form 1,4-adduct **6** (Scheme 2).

Scheme 2



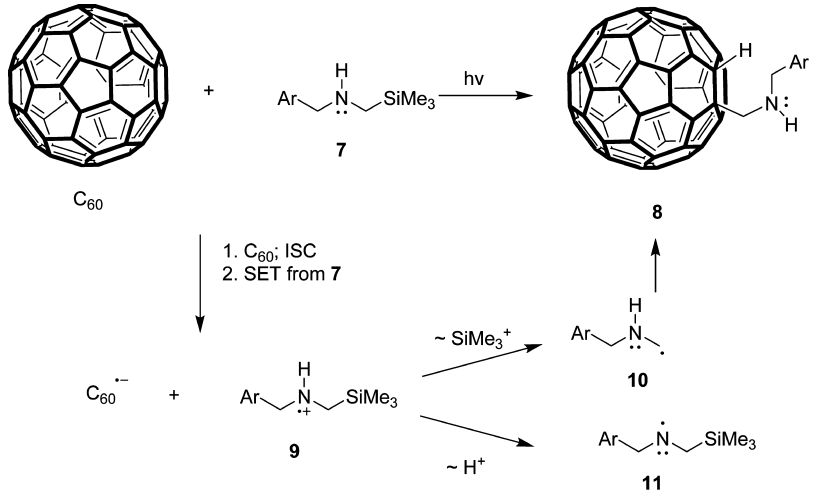
The high propensity of secondary aminium radicals to undergo N−H deprotonation or addition prevents the utilization of SET photochemical reactions between secondary amines and acceptors to prepare secondary aminomethyl adducts. For example, this limitation prohibits the ready preparation of aminomethyl-1,2-dihydrofullerene adducts, which possess an amine site for ensuing amide bond-forming processes that could lead to potentially useful, diversely functionalized fullerenes. Pertinent to this conclusion are the results of recent efforts by Nakamura,[52] Gan,[53] and others,[54] which demonstrate that SET-promoted photochemical reactions between secondary amines and fullerenes produce mono- and multiaminated fullerene derivatives exclusively.

The investigation described below was designed to explore SET-promoted photoaddition reactions of secondary *N*-trialkylsilylmethyl-amines **7** with fullerenes C_{60} (Scheme 3) to determine if these processes lead to efficient formation of secondary aminomethyl-1,2-fullerene adducts. We reasoned that the presence of α-trialkylsilyl groups in aminium radicals (**9** in Scheme 3) formed by SET oxidation could have the propensity to undergo desilylation more rapidly than N−H deprotonation or addition processes. If so, SET-promoted photoreactions of the α-trialkylsilyl-substituted secondary amines should take place by a pathway in which formation of aminomethyl radicals **10** rather than aminyl radicals **11** occurs preferentially or exclusively and leads to production of aminomethyl-1,2-fullerene adducts **8**. The observations made in the effort described below demonstrate the validity of this proposal. Specifically, photochemical reactions between secondary *N*-trimethylsilylmethyl-*N*-benzylamines and C_{60} do indeed efficiently generate aminomethyl-1,2-dihydrofullerene adducts. To the best of our knowledge, the observations made in this effort are the first to show that aminomethyl radicals can be generated in a chemoselective manner from secondary aminium radicals. Moreover, the photochemical methodology developed for introduction of secondary and perhaps primary and unsubstituted amine groups into electron acceptors has the potential of serving as a key element in strategies employed to design synthetic routes exemplified by the preparation of uniquely functionalized fullerenes.

RESULTS AND DISCUSSION

Photoreactions of C_{60} with Secondary *N*-Trimethylsilylmethyl-*N*-benzylamines. The aryl ring-substituted secondary *N*-trimethylsilylmethyl-*N*-benzylamines **12**−**22** (Scheme 4) utilized in this study were prepared by using *N*-alkylation

Scheme 3



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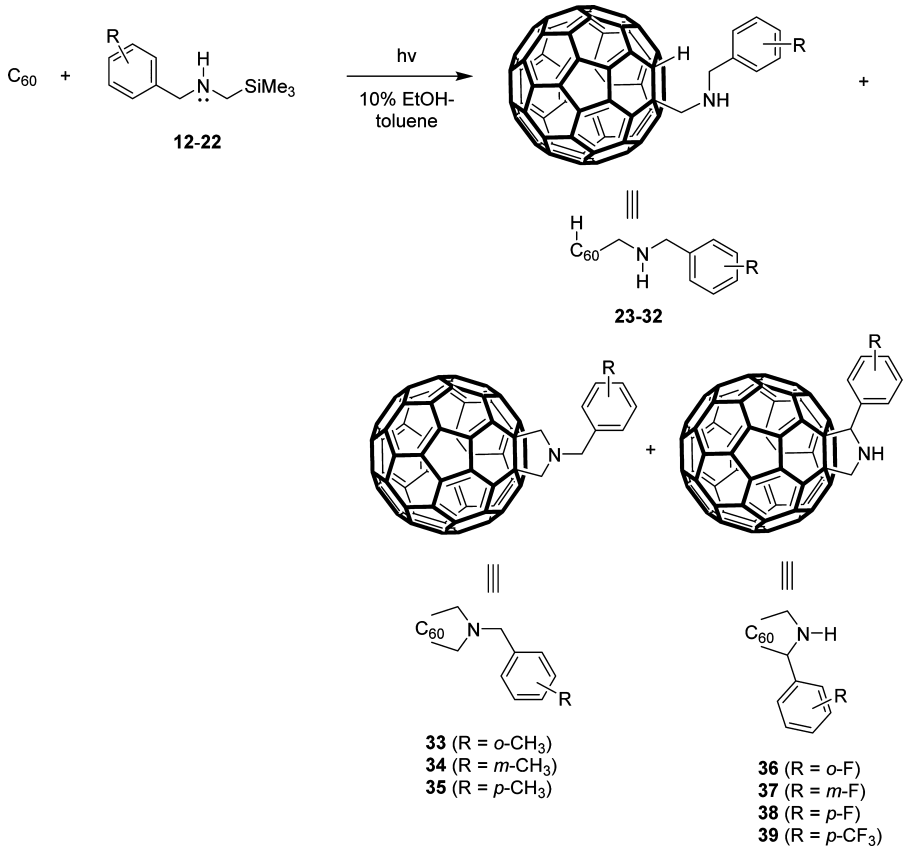
Scheme 4



Amine	Aminomethyl-1,2-dihydrofullerene	R
12	**23**	H
13	**24**	*o*-Me
14	**25**	*m*-Me
15	**26**	*p*-Me
16	**27**	*o,p*-diMe
17	**28**	*p*-OMe
18	**29**	*o*-F
19	**30**	*m*-F
20	**31**	*p*-F
21	-	*o,p*-diF
22	**32**	*p*-CF_3

reactions of the corresponding benzylamines with iodomethyltrimethylsilane. For promoting photoaddition reactions, N_2-purged, 10% EtOH-toluene solutions containing C_{60} (0.28 mmol) and the secondary amines **12**–**22** (0.56 mmol) were irradiated (>300 nm) for the time periods shown in Table 1. These photoreactions generate the products depicted in Scheme 4 in yields given in Table 1. It should be noted that irradiation of air-purged solutions of these substances does not give rise to photoadduct formation.

As can be seen by viewing the results shown in Scheme 4 and Table 1, 20 min photoirradiation of 10% EtOH-toluene solution of C_{60} and *N*-trimethylsilylmthyl-*N*-benzylamine **12** leads to exclusive production of aminomethyl-1,2-dihydrofullerene **23** (entry 1). Moreover, photoreactions of C_{60} and the *o,p*-di-Me and the *p*-OMe-substituted *N*-trimethylsilylmethyl-*N*-benzylamines **16** and **17** generate the aminomethyl adducts **27** and **28**, respectively, as a sole product in high yield (Table 1, entries 5 and 6). Likewise, irradiation of solutions of C_{60} and amines **13**–**15**, which contain *o*-, *m*-, and *p*-Me substituents, gives rise to the formation of the respective aminomethyl-1,2-dihydrofullerenes **24**–**26** mainly, along with lesser amounts of the corresponding symmetric fulleropyrrolidines **33**–**35**. (Table 1, entries 2–4).

The nature of photoreactions of C_{60} with electron-withdrawing group-substituted *N*-trimethylsilylmethyl-*N*-benzylamines were found to be different from those of their electron-donating-substituted analogues. Specifically, photoreactions of C_{60} with *o*-, *m*-, and *p*-F, *o,p*-di-F, and *p*-CF_3 substituted *N*-trimethylsilylmethyl-*N*-benzylamines **18**–**22** require longer irradiation times to produce high conversions (Table 1, entries 7–13). Furthermore, the yields of aminomethyl-1,2-dihydrofullerene adducts are lower than those arising from photoreactions of electron-donating-substituted analogues, and the unique unsymmetric fulleropyrrolidines **36**–**39** are generated as either minor or major products. Particularly interesting is the observation that shows that while reaction of C_{60} with the *p*-F substrate **20** produces aminomethyl-1,2-hydrofullerene **31** as a major product (49%) and asymmetric fulleropyrrolidine **38** as a minor adduct (7%) when a short irradiation time (1 h) is used, irradiation for a longer time (2 h)

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Table 1. Products and yields of photoaddition reactions of C_{60} (0.28 mmol) and the secondary *N*-trimethylsilylmethyl-*N*-benzylamines 12-22 (0.56 mmol) in 10% EtOH-toluene

entry	amine	irradiation time (min)	conversion (%)[a]	product (%)[b]
1	**12**	20	90	**23** (58)
2	**13**	20	95	**24** (61), **33** (1)
3	**14**	20	91	**25** (51), **34** (2)
4	**15**	20	96	**26** (59), **35** (3)
5	**16**	30	86	**27** (55)
6	**17**	20	95	**28** (73)
7	**18**	120	82	**29** (15), **36** (30)
8	**19**	120	80	**30** (10), **37** (32)
9	**20**	60	79	**31** (49), **38** (7)
10	**20**	120	85	**31** (18), **38** (47)
11	**21**	480	0	*c*
12	**22**	120	65	**32** (18), **39** (24)
13	**22**	300	87	**32** (2), **39** (60)

[a]Percent conversion is based on recovered C_{60}. [b]Isolated yields. [c]No photoproduct formed.

gives rise to predominant formation of unsymmetric fulleropyrrolidine **38**. (Table 1, entries 9 and 10) Similarly, although 1 h photolysis of a solution of C_{60} containing *p*-CF_3-substituted *N*-trimethylsilylmethyl-*N*-benzylamine **22** generates a mixture of aminomethyl adduct **32** (18%) and symmetric fulleropyrrolidine **39** (24%), 5 h irradiation gives rise to exclusive production of **39** (60%) (Table 1, entries 12 and 13). Finally, in contrast to the other amines, *o*,*p*-di-F-substituted benzylamine **21** does not undergo photoaddition reactions with C_{60} even when much longer irradiation times are employed (8 h).

Structural assignments to the aminomethyl-1,2-dihydrofullerenes and symmetric and unsymmetric fulleropyrrolidines formed in the reactions displayed in Scheme 4 were made by using ^{1}H and ^{13}C NMR, IR, UV−visible spectroscopy, and HRMS spectrometry (Supporting Information) as well as by comparison of the data to those of previously characterized analogues. In particular, in the ^{1}H NMR spectra of aminomethyl-1,2-dihydrofullerenes **23**−**32**, ^{1}H signals for protons directly bonded to the fullerene core are present in the 6.7−7.0 ppm region.[55,56] In ^{13}C NMR spectra of these substances, resonances for the fullerene sp^3 carbons occur at ∼70 ppm, and the methylene carbons bonded to the fullerene core resonate at ∼60 ppm. The IR spectra of **23**−**32** contain broad peaks in the 3000 cm^{-1} region that correspond to N−H stretching vibrations. The ^{1}H NMR spectra of the asymmetric fulleropyrrolidines **36**−**39**, derived from F- and CF_3-substituted benzylamines **18**−**20** and **22**, contain signals for diastereotopic methylene protons at approximately 4.8 and 5.1 ppm that appear as AB-quartets owing to the presence of stereogenic centers. Moreover, the N−H and methine proton resonances occur as singlets in the 5.7−6.0 ppm region. In the ^{13}C NMR spectra of **36**−**39**, the methylene, methine, and two sp^3 carbons on the fullerene cores resonate in the 61.0−78.0 ppm region. The IR spectra of these substances contain broad peaks in the 3000 cm^{-1} region. Finally, the symmetric fulleropyrrolidines **33**−**35**, derived from the corresponding benzylamines **13**−**15**, have more simple ^{1}H- and ^{13}C-NMR spectra that reflect their symmetric nature. For instance, two sets of nonequivalent methylene protons in each resonate as singlets at approximately 4.2−4.5 ppm in the ^{1}H NMR spectra, and the associated carbons resonate at approximately 57−70 ppm in the ^{13}C NMR spectra. In addition, the NMR spectra of **33**−**35** match those of known *N*-alkyl-fulleropyrrolidines well.[53,57] Finally, the UV−visible absorption spectra of all of the photoproducts contain absorption bands with maxima at approximately 433−436 nm that are characteristic of adducts generated by 1,2-addition across the [6,6]-juncture of C_{60}.[22,55,56]

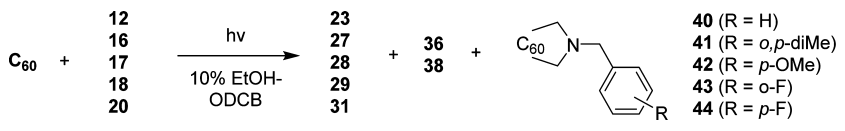
Solvent Dependence of Photoproduct Distributions. In an earlier study,[25a] we explored the effects of the EtOH content of EtOH-toluene solvent mixtures on the efficiencies of photoaddition reactions of C_{60} and tertiary *N*-trimethylsilylmethyl-substituted amines. The results showed that the presence of polar protic EtOH is required to enable the photoaddition reactions to occur efficiently. This effect is a consequence of the ability of EtOH to promote desilylation of intermediate aminium radicals and to protonate fullerene anions arising by coupling of aminomethyl radicals to the fullerene radical anions (Scheme 3). Because C_{60} has a limited range of solvents in which it is soluble, we carried out a brief study aimed at exploring the photoaddition reactions of this fullerene with secondary *N*-trimethylsilylmethyl-*N*-benzylamines in 10% EtOH-*o*-dichlorobenzene (ODCB) solutions. Initial studies were conducted using the methyl-substituted *N*-trimethylsilylmethyl-*N*-benzylamines **14** and **15**. Quite unexpectedly, product distributions arising from these photoreactions are dramatically different from those produced in reactions of the same substrates in 10% EtOH-toluene. Specifically, irradiation of 10% EtOH-ODCB solution of **14** and **15** containing C_{60} generates symmetric fulleropyrridines **34** and **35**, respectively (Scheme 5, Table 2, entries 2 and 3).

Table 2. Products and Yields of Photoaddition Reactions of C_{60} with *N*-Trimethylsilylmethyl-*N*-benzylamines 12, 14−18, and 20 in 10% EtOH-ODCB[a]

entry	amine	irradiation time (min)	conversion (%)[b]	product (%)[c]
1	**12**	20	71	**23** (10), **40** (33)
2	**14**	20	75	**25** (3), **34** (41)
3	**15**	20	87	**26** (2), **35** (56)
4	**16**	30	75	**27** (7), **41** (41)
5	**17**	20	84	**28** (5), **42** (42)
6	**18**	420	89	**29** (18), **36** (28), **43** (9)
7	**20**	120	26	**31** (1), **38** (4), **44** (11)
8	**20**	420	88	**29** (15), **36** (25), **44** (19)

[a]Amine/C_{60} is 0.56/0.28 mmol in 220 mL of 10% EtOH-ODCB. [b]Percent conversions are based on recovered C_{60}. [c]Isolated yields.

Scheme 5



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For the generality of this unusual solvent effect to be determined, photoaddition reactions of 10% EtOH-ODCB solutions containing C_{60} and other *N*-trimethylsilylmethyl-*N*-benzylamines, including **12**, **16**−**18**, and **20**, were carried out. The results (Scheme 5 and Table 2) show that, unlike photoreactions of these amines in 10% EtOH-toluene, those in 10% EtOH-ODCB give rise to the formation of the respective symmetric fulleropyrrolidines **40**−**44**.

Preferential formation of symmetric fulleropyrrolidines in photoreactions of secondary *N*-trimethylsilylmethyl-*N*-benzylamines **12**−**17** in 10% EtOH-ODCB is both surprising and interesting. For the mechanistic pathway involved in the production of these products to be explored, photoreactions of C_{60} with amine **15** were carried out under various conditions. The results show that no photoproducts are generated when EtOH is absent from the solvent or when the solution is purged with molecular oxygen. Moreover, in a manner that is consistent with the data displayed in Table 2, the ratios of the yields of aminomethyl-1,2-dihydrofullerene **26** and symmetric fulleropyrrolidine **35** dramatically change from 6:1 to 1:3 when the solvent is changed from 10% EtOH-toluene to 10% EtOH-ODCB.

Substituent Effects on Photoreaction Efficiencies. The observations described thus far show that the irradiation times required to bring about high conversions of C_{60} in photoreactions with the *N*-trimethylsilylmethyl-*N*-benzylamines are dependent on the electronic properties of the aryl ring substituent. For quantitative information regarding this effect to be acquired, relative quantum yields (Φ_{rel}) of the processes were determined. For this purpose, nitrogen-purged 10% EtOH-toluene solutions (10 mL) containing C_{60} (0.17 mM) and the amines (0.35 mM) were simultaneously irradiated for a fixed time period that promotes an average substrate conversion below ∼10%. Photoproduct yields were then determined by utilizing HPLC analysis of crude photolyzates and transformed into relative quantum efficiencies (Φ_{rel}) by setting the Φ_{rel} for reaction of **22** to be unity. The results (Table 3) show that the efficiencies of photoreactions of the arene ring electron-donating group (Me and OMe)-substituted *N*-trimethylsilylmethyl-*N*-benzylamines are significantly higher than those of the non- and electron-withdrawing (F and CF_3)-substituted analogues.[25b] Importantly, the nontrimethylsilyl-containing amine, *N*-methyl-*N*-benzylamine, is unreactive under the conditions employed.

Table 3. Relative Quantum Yields (Φ_{rel}) of Photoaddition Reactions of C_{60} with *N*-Trimethylsilylmethyl-*N*-benzylamines[a]

substrate	Φ_{rel}
12	6.6
15	6.8
17	10
20	4.9
21	1
N-methyl-*N*-benzylamine	

[a]Fixed time irradiations of N_2-purged 10% EtOH-toluene solutions containing amine and C_{60} at respective concentrations of 0.35 and 0.17 mM.

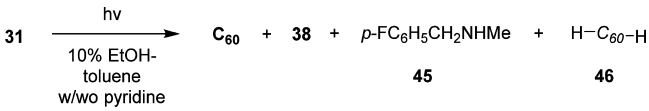
To probe the possible origin of the effect of substituents on reaction efficiencies, cyclic voltammetry measurements were performed to assess the electron donor propensities of the amines. Inspection of the data shows that the amines are oxidized irreversibly and that their oxidation peak potentials (Table 4) are nearly equal. Consequently, the effects of substituents on efficiencies are not a consequence of varying electron donation abilities of the amines.

Table 4. Oxidation Peak Potentials (E_p) of *N*-Trimethylsilylmethyl-*N*-benzylamines 12, 15, 20, and 21

amine	E_p vs Fc/Fc^+ (V)
12	1.09
15	0.95
20	1.09
21	1.07

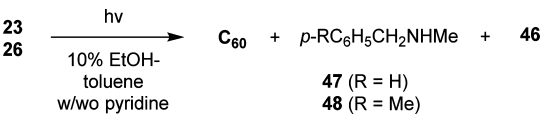
Photoreactions of Aminomethyl-1,2-dihydrofullerene Adducts. Additional studies were performed to obtain information regarding the origin of the unsymmetric fulleropyrrolidines and, in particular, to see if these substances are produced by secondary photoreactions of the initially formed aminomethyl-1,2-dihydrofullerenes, as the results displayed in Table 1 suggest. For this purpose, photoreaction of aminomethyl-1,2-dihydrofullerene **31**, derived from the *p*-F-substituted secondary *N*-trimethylsilylmethyl-*N*-benzylamine **20**, was carried out under various solvent and additive conditions. The results show that, upon irradiation of a 10% EtOH-toluene solution, **31** gradually disappears along with simultaneous formation of fulleropyrrolidine **38** and small amounts of C_{60} and *N*-methyl-*N*-benzylamine **45** (Scheme 6, Figure S1a). In contrast, when the solution contains 2 mol equiv of pyridine as a base, irradiation brings about more efficient conversion of **31** to **38**, and 1,2-dihydrofullerene **46**[58] is produced as a minor product (Figure S1b). Importantly, **31** does not react when irradiated in pure toluene or when the 10% EtOH-toluene solution is oxygenated.

Scheme 6



Photoreactions of the respective non- and methyl-substituted aminomethyl-1,2-dihydrofullerenes **23** and **26** in 10% EtOH-toluene solutions were also investigated. As can be seen from viewing the plots displayed in Figure S2, although photoreactions of **23** and **26** in the absence of pyridine generate only C_{60} and the corresponding desilylated amines **47** and **48**, those carried out in the presence of pyridine predominantly form 1,2-dihydrofullerene **46** (Scheme 7). Importantly, in these cases, the analogous unsymmetric fulleropyrrolidines are not produced. The results of these experiments show that the symmetric fulleropyrrolidines **33**−**35** are not produced in secondary photoreactions of the respective arene ring electron-donating group-substituted aminomethyl-1,2-dihydrofullerenes

Scheme 7



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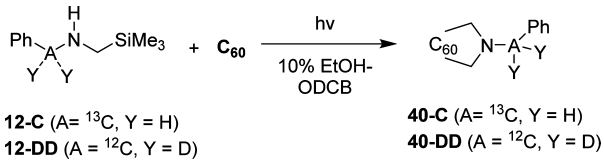
and that 1,2-dihydrofullerene **46** is generated from the aminomethyl-1,2-dihydrofullerene adducts when the mild base pyridine is present.

Exploring the Origin of the Symmetric Fulleropyrrolidines. As mentioned above, formation of the symmetric fulleropyrrolidines in the reactions described above is both not predicted and unusual. Several experiments were carried out to ascertain the origin of the second methylene group in these substances. Although unlikely, one source could be the benzylic center in the secondary *N*-trimethylsilylmethyl-*N*-benzylamines. This possibility was unambiguously ruled out based on observations made in studies with the ^{13}C- and d_2-labeled amines **12-C** and **12-DD** (Scheme 8). NMR analysis of the

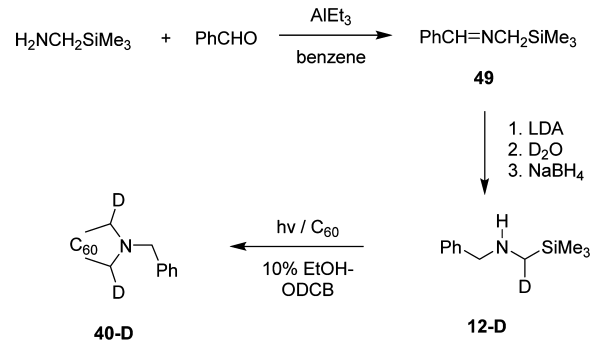
Scheme 8



symmetric fulleropyrrolidines arising from irradiation of 10% EtOH-ODCB solutions of these substrates show that they contain the ^{13}C and deuterium labels at the benzylic carbon exclusively (i.e., **40-C** and **40-DD**).

The only other source for the second methylene group in the symmetric fulleropyrrolidines is the trimethylsilyl-linked methylene group in the amine substrates. This conclusion gains support from observations made in studies with selectively deuterium-labeled *N*-trimethylsilylmethyl-*N*-benzylamine **12-D**, which contains 13% of a single deuterium label at the trimethylsilyl-linked methylene group. (Scheme 9). This

Scheme 9

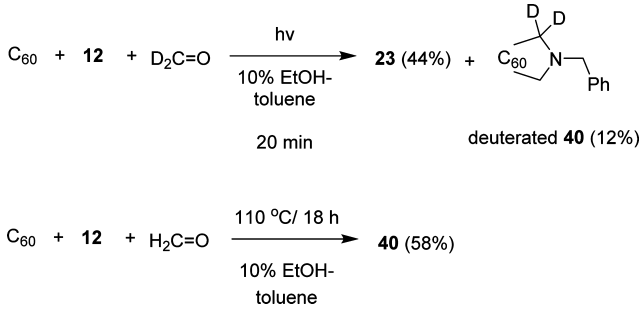


substance was generated by a sequence involving synthesis and reaction of *N*-trimethylsilylmethyl-benzaldimine **49**[59] with LDA to promote formation of the corresponding azaallyl anion. Reaction of the anion with D_2O followed by reduction of the aldimine with $NaBH_4$ produces **12-D**, whose extent and regioselectivity of deuterium incorporation was determined by using ^1H NMR analysis, which shows that the $PhCH_2$:Me_3SiCH_2 methylene proton ratio is 2:1.74. Photoreaction of **12-D** in 10% EtOH-ODCB was observed to produce the deuteriated fulleropyrrolidine **40-D**, which H^1 NMR analysis reveals has a $PhCH_2$:pyrrolidine ring methylene proton ratio of 2:3.48. The findings clearly demonstrate that the extra methylene groups in the fulleropyrrolidines originate from the trimethylsilyl-linked methylene groups (Me_3SiCH_2) of the amine substrates.

Another finding, which is in accordance with the proposed origin of the second methylene group in the fulleropyrrolidine products, is that benzylamine and its *p*-Me derivative are generated in respective 2 h photoreactions of the *N*-trimethylsilylmethyl-*N*-benzylamines **12** and **15** (0.35 mM) with C_{60} (0.17 mM) in 10% EtOH-ODCB. The result demonstrates that the Me_3SiCH_2 in the amine substrate is lost in the photochemical process, most likely through a pathway involving oxidative formation of an iminium ion intermediate followed by transfer of formaldehyde or its gem-diamine equivalent (see Discussion below).

Information regarding the relationship between formaldehyde and the generation of the fulleropyrrolidine comes from analysis of products formed in the photoreaction of a mixture of C_{60} (0.28 mmol), *N*-trimethylsilylmethyl-*N*-benzylamine **12** (0.56 mmol), and $D_2C{=}O$ (0.56 mmol) in 10% EtOH-toluene (Scheme 10). ^1H NMR analysis of symmetric fulleropyrrolidine

Scheme 10



40 produced in this process shows that it has a $PhCH_2$:pyrrolidine ring methylene proton ratio of 2:2. Thus, the CD_2 group of bis-deuterio-formaldehyde ($D_2C{=}O$) becomes one of the two methylene groups in the pyrrolidine ring of **40**. Finally, thermal (dark) reaction of a mixture of *N*-trimethylsilylmethyl-*N*-benzylamine **12**, C_{60}, and formaldehyde ($H_2C{=}O$) in 10% EtOH-toluene at 110 °C for 18 h leads to exclusive formation of **40** in 58% yield.

The study described above was designed to explore the viability and mechanistic features of SET-promoted photoreactions of acceptors with secondary *N*-trimethylsilylmethyl-*N*-benzylamines that lead to C−C bond-forming aminomethylation processes. The results of this effort demonstrate that aminium radicals generated by SET from the α-trimethylsilyl-substituted secondary amines undergo silophile-induced desilylation. This process efficiently produces aminomethyl radicals, which are intermediates in pathways that lead to C−C bond formation and production of aminomethyl adducts. This is a significant finding because it contrasts with those arising from other investigations, which show that SET-promoted reactions of secondary amines with aromatic electron acceptors typically generate amination products resulting from N−C bond formation (see above). Amination reactions occur preferentially in these cases because the rates of both N−H deprotonation and arene addition of aminum radicals derived from secondary amines (see Scheme 2) are larger than those of α-CH deprotonation, which would produce aminomethyl radicals. Consequently, observations made in the current effort demonstrate for the first time that the regiochemical course of SET photoreactions of secondary amines can be changed to favor aminomethylation over amination by simply incorporating α-trimethylsilyl substituents in the amine substrate. Several

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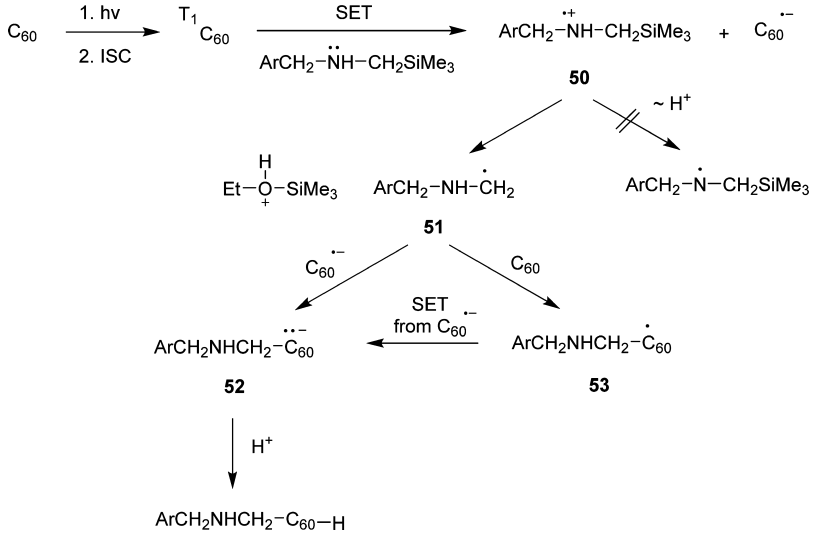
Scheme 11



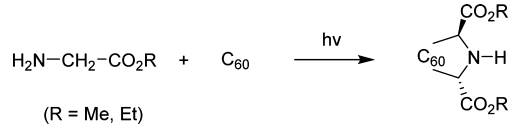
of the more significant observations made in this study are discussed below.

Mechanistic Pathways for Aminomethyl-1,2-dihydrofullerene Formation. The mechanistic route followed in photoreactions between secondary *N*-trimethylsilylmethyl-*N*-benzylamines is initiated by well-documented[60] SET to the triplet ($^{T1}C_{60}$) excited state of fullerene. Owing to the fact that the concentrations of amines used in the photoreaction are in the mM range, it is unlikely that SET quenching of the singlet excited state ($^{S1}C_{60}$) of fullerene by the amines takes place. At these concentrations, bimolecular SET quenching, even when it occurs at a diffusion controlled rate (10^9 M^{-1} s^{-1}), would not be competitive with intersystem crossing (ISC) to form $^{T1}C_{60}$ (k_{ISC} = ~2 × 10^9 s^{-1}).[61] As a result, the initial SET step in the pathway (Scheme 11) produces triplet radical ion pairs comprised of aminium radicals **50** and the C_{60} radical anion ($C_{60}^{\bullet-}$).

α-Trimethylsilyl-substituted tertiary aminium radical are known[35] to undergo alcohol- and water-promoted desilylation to form aminomethyl radicals with exceptionally large rates that exceed those of *α*-CH deprotonation. The results of the current study show that secondary *N*-trimethylsilylmethyl-aminium radicals, like **50**, also rapidly transfer silyl groups to EtOH, a solvent component that is required for the success of these photoaddition reactions. This process forms aminomethyl radicals **51** along with protonated EtO^+HSiMe_3. Two possible routes could be operating in the conversion of radical **51** to the aminomethyl-1,2-dihydrofullerene adduct. One involves coupling with $C_{60}^{\bullet-}$ followed by protonation of resulting anion **52**. Another pathway for formation of the adduct begins with the addition of **51** to C_{60} to formthe radical **53**. This process, which has precedence in the addition of hydroxymethyl[62] and benzyl[63] radicals to fullerene, is perhaps more reasonable owing to the exceedingly low concentrations of $C_{60}^{\bullet-}$ vs C_{60} that are present in the reaction mixture. This alternative route would be terminated by SET from $C_{60}^{\bullet-}$ to **53**, producing anion **52** that is the precursor of the aminomethyl adduct. It should be noted that the lifetime of $C_{60}^{\bullet-}$ produced in the initial SET step is likely to be significantly long owing to the weakly acidic nature of the photoreaction reaction medium and the fact that the fullerene radical anion is a weak base. The latter conclusion derives from observations made in independent electrochemical studies by Niyazymbetov[64] and Cliffel,[65] which show that the pK_a of H–$C_{60}^{\bullet}$ is 9 in DMSO and 4 in ODCB. Finally, on the basis of the electrochemical and pK_a data, it is expected that SET from $C_{60}^{\bullet-}$ to **53** to form C_{60} and anion **52** should be thermodynamically favorable.

Formation of Symmetric Fulleropyrrolidines. Owing to its relevance to a number of observations made in past studies and the general mechanistic and synthetic implications of the current effort, the route for formation of the symmetric fulleropyrrolidines is of interest. Earlier independent investigations by Skanji[66] and Gan[67] demonstrated that visible light irradiation of mixtures of C_{60} and methyl or ethyl glycinate in the presence of O_2 leads to the formation of fulleropyrrolidine bis-esters (Scheme 12).

Scheme 12



This process is closely related to the symmetric fulleropyrrolidine forming reactions of electron-donating-substituted *N*-trimethylsilylmethyl-*N*-benzylamines. Specifically, we observed that irradiation of solutions containing these secondary amines and C_{60} generates symmetric fulleropyrrolidines **58** (Scheme 13) as minor products when the solvent is 10% EtOH-toluene and major adducts when the solvent is 10% EtOH-ODCB. In studies aimed at determining the mechanistic origin of these cyclic adducts, we demonstrated that the extra methylene group in the **58** originates from the trimethylsilyl-linked methylene group in the amine substrate.

A mechanistic pathway for this process, which is compatible with this observation and the results of earlier studies of dipolar cycloaddition reactions of both C_{60}[7a,68] and azomethine ylide-forming reactions of secondary *N*-trimethylsilylmethyl-substituted amines,[69] is shown in Schemes 13. The key step in this route is SET oxidation by C_{60} of aminomethyl radical intermediate **51** generated by desilylation of the corresponding aminium radical. This process should be thermodynamically favorable owing to the fact that the oxidation potential of **51** is

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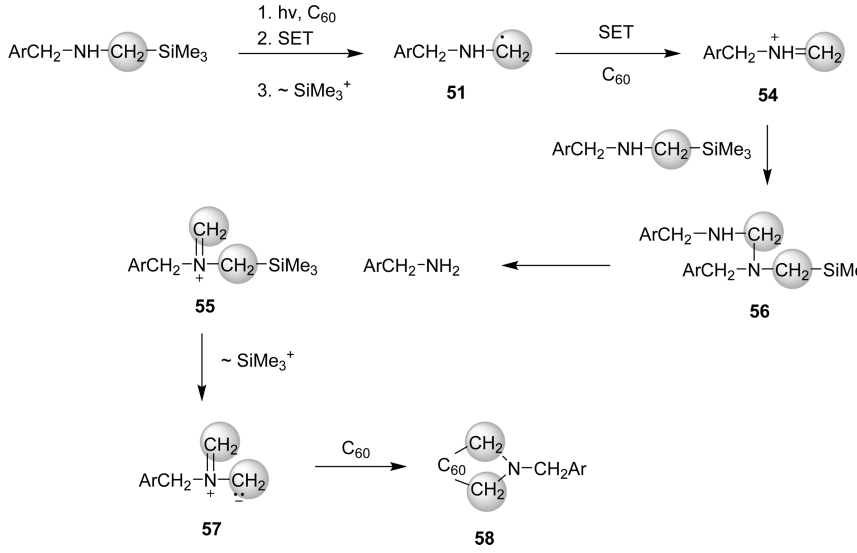
Scheme 13

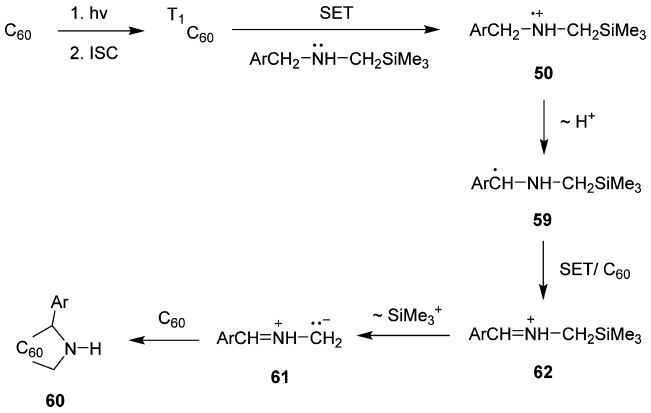


in the range of −1 V (vs SCE)[70] and the reduction potential of C_{60} is approximately +1 V (vs SCE).[64,71] Iminium ion **54** formed in this manner and then reacts with the secondary *N*-trimethylsilylmethyl-*N*-benzylamine to form gem-diamine **56** that loses benzylamine to produce the trimethylsilyl-substituted iminium ion **55**. Well-documented[69] desilylation of **55** then generates azomethine ylide **57**, which through Prato-like[68] 1,3-dipolar cycloaddition to C_{60} produces symmetric fulleropyrrolidine **58**.

A potentially interesting relationship exists between the pathways for formation of the aminomethyl-1,2-dihydrofullerene and symmetric fulleropyrrolidines adducts. Specifically, both processes involve key reactions between aminomethyl radical **51** and C_{60}, one potentially involving radical addition (Scheme 11) and the other SET (Scheme 13). In fact, the SET-promoted route between **51** and C_{60} might actually lead to formation of the same adduct radical **53**, shown in Scheme 10, via polar addition of $C_{60}^{\bullet-}$ to the resulting iminium ion **54**. However, a major difference between the processes is that one forms neutral radicals (**53**) and the other charged intermediates (**54**). Although it is too early to speculate with full confidence, the enhancement in the efficiency of symmetric fulleropyrrolidine formation caused by a change in the solvent from 10% EtOH-toluene to 10% EtOH-ODCB might a consequence of the differences in the radical versus ionic nature of these two processes. Specifically, ODCB is a more polar solvent than is toluene as reflected in their respective dielectric constants of 9.93 and 2.38 D. As a result, the symmetric fulleropyrrolidine forming processes that begin with SET to generate radical ion pairs might be facilitated in the more polar ODCB.

Formation of Unsymmetric Fulleropyrrolidines. The final observation made in the investigation described above that is worthy of brief discussion is the formation unsymmetric fulleropyrrolidines in photoreactions of specific secondary amines with C_{60}. In a manner that is similar to observations made in our earlier studies,[25] these adducts are produced as major products in photoreactions of only *N*-trimethylsilylmethyl-*N*-benzylamines containing electron-withdrawing substituents on the phenyl ring. Following earlier proposals made by Foote[72] and Baciocchi,[73] we suggested that cycloadducts of this type are produced in photoreactions of amines and C_{60} through a route involving the intermediacy of singlet oxygen produced by energy transfer from $^{T1}C_{60}$. However, because the concentrations of O_2 are low in the N_2-purged solution used in the photoreactions described above, the alternate pathway displayed in Scheme 14 should be considered. In this route,

Scheme 14



deprotonation of the benzylic hydrogen in aminium radical **50**, generated by SET from the secondary amine to $^{T1}C_{60}$, takes place competitively with desilylation. It is anticipated that the CH acidities of the benzylic protons in these aminium radicals would be enhanced by electron-withdrawing groups on the phenyl ring, which is consistent with the fact that this process is unique to an electron-withdrawing-substituted substrate. Oxidation of the formed aminomethyl radical **59** by thermodynamically favored SET to C_{60} then generates the iminium ion precursor (**62**) of azomethine ylide **61**, which upon cycloaddition to C_{60} forms unsymmetric fulleropyrrolidine **60**.

Another way in which unsymmetric fulleropyrrolidines are formed is through secondary photoreaction of initially formed aminomethyl-1,2-dihydrofullerene adducts (**63** in Scheme 15). This process most likely takes place by initial homolytic C−C bond cleavage in the excited state of **63** to form the radical pair **64** and **65**. Disproportionation of this pair produces either *N*-methyl-benzylamine **69** and C_{60} or azomethine ylide **61**, the precursor of adduct **60**, and 1,2-dihydrofullerene **46** (H−C_{60}−

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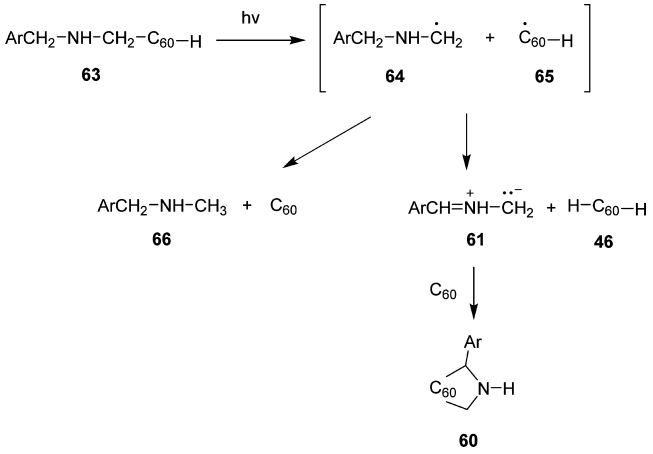
Scheme 15



H). It should be noted that **66**, C_{60}, and **46** are observed as products of this process and that this proposal does not account for the effect of pyridine on 1,2-dihydrofullerene **46** and fulleropyrrolidine adduct **60** formation.

CONCLUSIONS

In the current study, single electron transfer (SET)-promoted photoaddition reactions between C_{60} and secondary *N*-trimethylsilylmethyl-*N*-benzylamines were explored to determine if these substances would participate in new SET-promoted aminomethylation reactions. The results show that photoreactions of the electron acceptor C_{60} and *N*-trimethylsilylmethyl-*N*-benzylamines produce aminomethyl-1,2-dihydrofullerenes as major products through a pathway involving SET-promoted formation of secondary aminium radicals followed by preferential loss of the α-trimethylsilyl group rather than the N–H proton. The aminomethyl radicals formed in this manner then couple with C_{60} or its radical anion to form radical or anion precursors of the aminomethyl-1,2-dihydrofullerene products. In contrast to thermal and photochemical strategies developed previously, the new SET photochemical approach using α-trimethylsilyl-substituted secondary amines is both mild and efficient and, as a result, should be useful in broadening the library of substituted fullerenes. Moreover, the results should have an impact on the design of SET-promoted, C–C bond forming reactions. Specifically, introduction of an α-trimethylsilyl group leads to a change in the chemoselectivity of SET-promoted reactions of secondary amines with acceptors that typically favor aminium radical N–H deprotonation leading to N–C bond formation.

Finally, symmetric and unsymmetric fulleropyrrolidines are also generated in yields that are highly dependent on the electronic properties of substituents on the arene rings in amines, irradiation time, and solvent. For example, short period irradiation of 10% EtOH-toluene solution containing C_{60} and the secondary *N*-trimethylsilylmethyl-*N*-benzylamines, containing arene rings that are either unsubstituted or substituted with electron-donating groups (H, Me, and OMe), leads to high yielding formation of aminomethyl-1,2-dihydrofullerenes along with minor amounts of symmetric fulleropyrrolidines. In contrast, irradiation of 10% EtOH-toluene solution containing C_{60} and the amines with electron-withdrawing group-substituted (F and CF_3) arene rings promotes the production of aminomethyl-1,2-dihydrofullerenes along with minor amounts of unsymmetric fulleropyrrolidines. Moreover, symmetric fulleropyrrolidines are major products when 10% EtOH-ODCB solutions of C_{60} and the secondary *N*-trimethylsilylmethyl-*N*-benzylamines, containing either electron-withdrawing or electron-donating arene ring substituents, are irradiated.

EXPERIMENTAL SECTION

General. Commercially available fullerene C_{60} (>99% HPLC pure) was used as received. ^{1}H and ^{13}C NMR spectra (300 MHz) were recorded using $CDCl_3$ solutions, and chemical shifts are reported in parts per million relative to $CHCl_3$ (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) as an internal standard. High resolution (HRMS) mass spectra were obtained by using a quadrupole mass analyzer and electron impact ionization unless otherwise noted. All previously undescribed compounds were isolated as oils in >90% purity (NMR analysis) unless noted otherwise.

General Procedure for Synthesis of Secondary *N*-Trimethylsilylmethyl-*N*-benzylamines 12–22. Individual solutions of primary *N*-benzylamines (11 mmol) in acetonitrile (120 mL) containing K_2CO_3 (2.6 g, 18.7 mmol) and iodomethyltrimethylsilane (2.0 g, 9.3 mmol) were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were partitioned between water and CH_2Cl_2. The CH_2Cl_2 layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1:6–1:15) to yield the corresponding secondary *N*-trimethylsilylmethyl-*N*-benzylamines.

***N*-(2-Methylbenzyl)-1-(trimethylsilyl)methanamine 13.** ^{1}H NMR δ 0.07 (s, 9H), 2.11 (s, 2H), 2.35 (s, 3H), 3.85 (s, 2H), 7.13–7.20 (m, 3H), 7.29–7.32 (m, 1H); ^{13}C NMR δ −2.9, 18.7, 38.8, 54.9, 125.4, 126.7, 128.3, 129.9, 136.2, 136.9; HRMS (EI) *m*/*z* 207.1441 (M^+, $C_{12}H_{21}NSi$ requires 207.1443).

***N*-(3-Methylbenzyl)-1-(trimethylsilyl)methanamine 14.** ^{1}H NMR δ 0.1 (s, 9H), 2.10 (s, 2H), 2.35 (s, 3H), 3.92 (s, 2H), 7.08–7.26 (m, 4H); ^{13}C NMR δ −2.2, 21.3, 35.9, 54.0, 124.6, 126.4, 128.8, 129.2, 130.0, 138.7; HRMS (FAB) *m*/*z* 208.1521 (M + 1, $C_{12}H_{22}NSi$ requires 208.1522).

***N*-(4-Methylbenzyl)-1-(trimethylsilyl)methanamine 15.** ^{1}H NMR δ 0.03 (s, 9H), 2.04 (s, 2H), 2.33 (s, 3H), 3.75 (s, 2H), 7.13 (d, 2H, *J* = 8.1 Hz), 7.19 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR δ −2.6, 21.0, 39.4, 57.8, 128.0, 128.9, 136.2, 137.5; HRMS (FAB) *m*/*z* 208.1524 (M + 1, $C_{12}H_{22}NSi$ requires 208.1522).

***N*-(2,4-Dimethylbenzyl)-1-(trimethylsilyl)methanamine 16.** ^{1}H NMR δ 0.11 (s, 9H), 2.16 (s, 2H), 2.36 (s, 3H), 2.38 (s, 3H), 3.81 (s, 2H), 7.03 (d, 1H, *J* = 6.3 Hz), 7.04 (s, 1H), 7.22 (d, 1H, *J* = 6.3 Hz); ^{13}C NMR δ −2.7, 18.8, 20.9, 39.7, 55.6, 126.2, 128.5, 131.0, 135.1, 136.3; HRMS (EI) *m*/*z* 221.1598 (M^+, $C_{13}H_{23}NSi$ requires 221.1600).

***N*-(2-Fluorobenzyl)-1-(trimethylsilyl)methanamine 18.** ^{1}H NMR δ 0.04 (s, 9H), 2.05 (s, 2H), 3.90 (s, 2H), 6.98–7.04 (m, 1H), 7.06–7.11 (m, 1H), 7.18–7.25 (m, 1H), 7.33–7.38 (m, 1H); ^{13}C NMR δ −2.7, 38.6, 50.5, 115.1 (d, J_{C-F} = 87 Hz), 123.9 (d, J_{C-F} = 14.1 Hz), 128.6 (d, J_{C-F} = 32.7 Hz), 130.5 (d, J_{C-F} = 19.2 Hz), 161.3 (d, $^1J_{C-F}$ = 975.6 Hz); HRMS (EI) *m*/*z* 211.1192 (M^+, $C_{11}H_{18}FNSi$ requires 211.1193).

***N*-(3-Fluorobenzyl)-1-(trimethylsilyl)methanamine 19.** ^{1}H NMR δ 0.05 (s, 9H), 2.04 (s, 2H), 3.78 (s. 2H), 6.88–6.94 (m, 1H), 7.03–7.08 (m, 2H), 7.21–7.29 (m, 1H); ^{13}C NMR δ −2.74, 39.4, 57.8 (d, J_{C-F} = 6.6 Hz), 113.4 (d, J_{C-F} = 84 Hz), 114.7 (d, J_{C-F} = 84 Hz), 123.5 (d, J_{C-F} = 11.1 Hz), 129.5 (d, J_{C-F} = 32.4 Hz), 143.4 (d, J_{C-F} = 27 Hz), 162.9 (d, $^1J_{C-F}$ = 975.3 Hz); HRMS (EI) *m*/*z* 211.1191 (M^+, $C_{11}H_{18}FNSi$ requires 211.1193).

***N*-(4-Fluorobenzyl)-1-(trimethylsilyl)methanamine 20.** ^{1}H NMR δ 0.02 (s, 9H), 2.00 (s, 2H), 3.73 (s, 2H), 6.95–7.00 (m, 2H), 7.22–7.27 (m, 2H); ^{13}C NMR δ −2.7, 39.3, 57.2, 114.9 (d, J_{C-F} = 83.7 Hz), 129.5 (d, J_{C-F} = 30.9 Hz), 136.2 (d, J_{C-F} = 12 Hz), 161.7 (d, $^1J_{C-F}$ = 970.8 Hz); HRMS (FAB) *m*/*z* 212.1273 (M + 1, $C_{11}H_{19}FNSi$ requires 212.1271).

***N*-(2,4-Difluorobenzyl)-1-(trimethylsilyl)methanamine 21.** ^{1}H NMR δ 0.02 (s, 9H), 2.01 (s, 2H), 3.84 (s, 2H), 6.72–6.83 (m, 2H), 7.28–7.36 (m, 1H); ^{13}C NMR δ −2.7, 38.4, 49.9 (d, J_{C-F} = 8.1

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Hz), 103.6 (t, J_{C-F} = 102 Hz), 111.0 (dd, J_{C-F} = 83.1 Hz, 14.4 Hz), 121.9 (d, J_{C-F} = 60 Hz), 131.3 (dd, J_{C-F} = 25.7 Hz, 37.5 Hz), 160.0 (dd, J_{C-F} = 985 Hz, 48 Hz), 161.1 (dd, J_{C-F} = 986.1 Hz, 47.4 Hz); HRMS (EI) m/z 229.1097 (M + 1, $C_{11}H_{17}F_2NSi$ requires 229.1098).

***N*-(4-(Trifluoromethyl)benzyl)-1-(trimethylsilyl)-methanamine 22.** ^{1}H NMR δ 0.03 (s, 9H), 2.01 (s, 2H), 3.83 (s, 2H), 7.41 (d, 2H, J = 8.1 Hz), 7.56 (d, 2H, J = 8.1 Hz); ^{13}C NMR δ −2.7, 39.5, 57.5, 125.2 (q, $^1J_{C-F}$ = 15 Hz), 128.3, 144.7; HRMS (FAB) m/z 262.1240 (M + 1, $C_{12}H_{19}F_3NSi$ requires 262.1239).

Synthesis of Isotope-Labeled *N*-α-Trimethylsilyl-*N*-benzylamines 12-C and 12-DD. To 15 mL of a MeCN solution of *N*-α-trimethylsilyl-amine (1.4 mmol) was independently added α,α-d_2- and α-^{13}C-labeled benzyl bromide (0.2 g, 1.2 mmol). The resulting solutions were stirred for 12 h at room temperature and concentrated in vacuo to give residues that were partitioned between water and EtOAc. The EtOAc layers were dried and concentrated in vacuo to afford residues that were subjected to silica gel column chromatography (EtOAc/hexane = 1:8) to yield the corresponding isotopically labeled *N*-α-trimethylsilyl-*N*-benzylamines **12-C** (156 mg, 69%) and **12-DD** (186 mg, 83%).

1-Phenyl-*N*-((trimethylsilyl)methyl)methanamine-^{13}C 12-C. ^{1}H NMR δ 0.05 (s, 9H), 2.06 (d, 2H, J = 3.3 Hz), 3.83 (d, 2H, $J_{H-^{13}C-H}$ = 134.1 Hz), 7.25−7.33 (m, 5H); ^{13}C NMR δ −2.7, 57.5, 58.3, 126.9, 128.1 (d, J = 11.1 Hz), 128.2 (d, J = 14.7 Hz), 139.7 (d, J_{C-C} = 181.2 Hz); HRMS (FAB) m/z 195. 1398 (M + 1, $C_{10}{}^{13}CH_{20}NSi$ requires 195.1399).

1-Phenyl-*N*-((trimethylsilyl)methyl)methan-d_2-amine 12-DD. ^{1}H NMR δ −0.03 (s, 9H), 1.98 (s, 2H), 7.17−7.26 (m, 5H); ^{13}C NMR δ −2.6, 39.2, 126.8, 128.1, 128.2, 140.3; HRMS (FAB) m/z 196.1489 (M + 1, $C_{11}CH_{18}D_2NSi$ requires 196.1491).

Synthesis of Deuterated *N*-Trimethylsilylmethyl-*N*-benzylamine 12-D. To a solution of $AlEt_3$ (25% hexane solution, 6.1 mL, 11.3 mmol) in dry benzene (20 mL) was added *N*-trimethylsilylmethylamine (1.17 g, 11.3 mmol). The solution was stirred for 30 min at room temperature, and then benzaldehyde (0.8 g, 7.5 mmol) was added. The resulting solution was stirred at reflux for 1.5 h and then cooled to room temperature. Ethanol (5 mL) and 10% sodium tartrate (20 mL) were added, and the resulting solution was partitioned between water and CH_2Cl_2. The combined CH_2Cl_2 layers were dried and concentrated in vacuo to give *N*-trimethylsilylmethyl-*N*-benzaldimine **49** (1.21 g, 84%).

To an LDA (7.8 mmol) solution in anhydrous THF (10 mL) was added *N*-α-trimethylsilyl-benzaldimine **49** (1.0 g, 5.2 mmol) at −78 °C, and the resulting solution was stirred for 1 h. Following warming to room temperature, excess D_2O was added, and the resulting solution was concentrated in vacuo to give a residue that was partitioned between water and CH_2Cl_2. The combined CH_2Cl_2 layers were dried and concentrated in vacuo to give the corresponding deuterated *N*-(trimethylsilylmethyl)imine (0.94 g, 94%).

To the solution containing the imine (1.0 g, 5.2 mmol) in dry THF (20 mL) was added $NaBH_4$ (0.2 g, 5.2 mmol). The solution was stirred at room temperature for 12 h and concentrated in vacuo to give a residue that was partitioned between water and CH_2Cl_2. The combined CH_2Cl_2 layers were dried and concentrated in vacuo to afford a residue that was subjected to silica gel column chromatography (EtOAc/hexane = 1:10) to yield *N*-α-trimethylsilyl-*N*-benzylamine **12-D** (0.53 g, 52%). Analysis of ^{1}H NMR δ peak integrations shows that ∼13% of *N*-trimethylsilylmethyl-*N*-benzylamine is deuterated (13% of **12-D**).

General Procedure for Photoreactions of C_{60} with Secondary *N*-Trimethylsilylmethyl-*N*-benzylamines. Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a flint glass filter (>300 nm) in a water-cooled quartz immersion well surrounded by a solution consisting of 10% EtOH-toluene or 10% EtOH-ODCB (220 mL), C_{60} (0.28 mmol), and one of the secondary *N*-trimethylsilylmethyl-*N*-benzylamines (**12**−**22**, 0.56 mmol). Each solution was purged with nitrogen before and during irradiation, which was carried out for the time periods given for each substance below. The photolyzates were concentrated, and the generated residues were triturated with $CHCl_3$ to recover C_{60}. The triturates were concentrated in vacuo to generate residues that were subjected to silica gel column chromatography (eluants given below) to obtain photoproducts.

Photoreaction of C_{60} with 12. In 10% EtOH-toluene solution: 20 min irradiation, 90% conversion, column chromatography (CS_2) to yield **23** (135 mg, 58%). In 10% EtOH-ODCB solution: 20 min irradiation, 71% conversion, column chromatography (CS_2) to yield **23** (23 mg, 10%) and **40** (79 mg, 33%).

23: ^{1}H NMR δ 4.42 (s, 2H), 4.50 (s, 2H), 6.91 (s, 1H), 7.33−7.38 (m, 1H), 7.43−7.48 (m, 2H), 7.64 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 54.6, 58.6, 62.3, 66.4, 127.3, 128.2, 128.6, 136.0, 136.4, 139.7, 140.3, 140.1, 141.4, 141.6, 141.7, 141.9, 142.2, 142.3, 142.8, 143.0, 144.3, 144.5, 145.1, 145.2, 145.3, 145.6, 145.9, 146.0, 146.1, 146.2, 146.4, 147.0, 147.1, 154.0, 154.1; HRMS (FAB) m/z 842.0973 (M + 1, $C_{68}H_{12}N$ requires 842.0970).

40: ^{1}H NMR δ 4.29 (s, 2H), 4.43 (s, 4H), 7.3−7.35 (m, 1H), 7.40−7.45 (m, 3H), 7.66 (d, 2H, J = 7.2 Hz); ^{13}C NMR δ 58.6, 67.2, 70.5, 128.7, 128.8, 136.1, 139.9, 141.6, 141.8, 142.0, 142.4, 142.8, 144.3, 145.0, 145.2, 145.5, 145.8, 145.9, 146.0, 147.1, 154.8; HRMS (FAB) m/z 854.0973 (M + 1, $C_{69}H_{12}N$ requires 854.0970).

Photoreaction of C_{60} with 13. In 10% EtOH-toluene solution: 20 min irradiation, 95% conversion, column chromatography (CS_2) to yield **24** (146 mg, 61%) and **33** (3 mg, 1%). In 10% MeOH-toluene solution: 20 min irradiation, 75% conversion, column chromatography (CS_2) to yield **24** (81 mg, 34%) and **33** (trace).

24: ^{1}H NMR δ 2.66 (s, 3H), 4.40 (s, 2H), 4.55 (s, 2H), 6.86 (s, 1H), 7.26−7.29 (m, 3H), 7.57−7.59 (m, 1H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 19.4, 52.7, 58.6, 62.7, 66.4, 126.0, 127.5, 128.8, 130.5, 135.9, 136.4, 136.5, 137.3, 140.0 (2C), 141.4, 141.5, 141.7, 141.8, 142.1, 142.3, 142.8, 142.9, 144.2, 144.4, 145.1 (2C), 145.3, 145.5, 145.9 (2C), 146.0, 146.1, 146.4, 146.9, 147.0, 147.1, 153.9, 154.0; HRMS (FAB) m/z 856.1122 (M + 1, $C_{69}H_{14}N$ requires 856.1126).

33: ^{1}H NMR δ 2.71 (s, 3H), 4.27 (s, 2H), 4.43 (s, 4H), 7.25−7.27 (m, 4H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 19.5, 57.0, 67.3, 70.2, 125.8, 127.6, 129.1, 130.4, 135.6, 135.8, 137.0, 139.8, 141.5, 141.6, 141.8, 142.2, 142.7, 144.1, 144.8, 145.0, 145.2, 145.6 (2C), 145.8, 146.8, 154.4; HRMS (FAB) m/z 868.1124 (M + 1, $C_{70}H_{14}N$ requires 868.1126).

Photoreaction of C_{60} with 14. In 10% EtOH-toluene solution: 20 min irradiation, 91% conversion, column chromatography (CS_2) to yield **25** (121 mg, 51%) and **34** (5 mg, 2%). In 10% EtOH-ODCB solution: 20 min irradiation, 75% conversion, column chromatography (CS_2) to yield **25** (6 mg, 3%) and **34** (99 mg, 41%).

25: ^{1}H NMR δ 2.45 (s, 3H), 4.37 (s, 2H), 4.49 (s, 2H), 6.91 (s, 1H), 7.13 (d, 1H, J = 7.2 Hz), 7.31 (t, 1H, J = 7.2 Hz), 7.40−7.43 (m, 2H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 21.5, 54.6, 58.5, 62.3, 66.4, 125.3, 128.0, 128.5, 129.0, 135.9, 136.3, 137.8, 139.6, 139.9, 140.0, 141.4, 141.5, 141.7, 141.8, 142.1, 142.3, 142.9, 144.2, 144.4, 145.0, 145.1, 145.3, 145.5, 145.9, 146.0, 146.1, 146.4, 147.0, 147.1, 153.9, 154.0; HRMS (FAB) m/z 856.1123 (M + 1, $C_{69}H_{14}N$ requires 856.1126).

34: ^{1}H NMR δ 2.46 (s, 3H), 4.25 (s, 2H), 4.42 (s, 4H), 7.15 (d, 1H, J = 7.5 Hz), 7.32 (t, 1H, J = 7.5 Hz), 7.44 (s, 1H), 7.48 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 21.5, 58.8, 67.3, 70.4, 125.8, 128.2, 128.5, 129.4, 136.0, 137.5, 137.8, 139.9, 141.6, 141.8, 142.0, 142.4, 142.8, 144.3, 145.0, 145.2, 145.4, 145.8, 146.0, 147.0, 154.6; HRMS (FAB) m/z 868.1122 (M + 1, $C_{70}H_{14}N$ requires 868.1126).

Photoreaction of C_{60} with 15. In 10% EtOH-toluene solution: 20 min irradiation, 96% conversion, column chromatography (CS_2) to yield **26** (140 mg, 59%) and **35** (7 mg, 3%). In 10% EtOH-ODCB solution: 20 min irradiation, 87% conversion, column chromatography (CS_2) to yield **26** (4 mg, 2%) and **35** (135 mg, 56%).

26: ^{1}H NMR δ 2.42 (s, 3H), 4.38 (s, 2H), 4.48 (s, 2H), 6.91 (s, 1H), 7.26 (d, 2H, J = 7.8 Hz), 7.53 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 21.2, 54.3, 58.7, 66.5, 128.3, 129.4, 136.1, 136.5, 136.9, 140.1, 140.2, 141.5 (2C), 141.7, 141.8, 142.0, 142.3, 142.4, 142.5, 143.1, 144.4, 144.6, 145.2 (2C), 145.3, 145.4, 145.7, 146.0, 146.1, 146.2, 146.3, 146.6, 147.1, 147.2, 147.3, 154.2, 154.3; HRMS (FAB) m/z 856.1123 (M + 1, $C_{69}H_{14}N$ requires 856.1126).

35: ^{1}H NMR δ 2.42 (s, 3H), 4.26 (s, 2H), 4.41 (s, 4H), 7.25 (d, 2H, J = 7.8 Hz), 7.56 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 21.2,

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58.4, 67.2, 70.3, 128.6, 129.2, 136.0, 136.9, 139.9, 141.6, 141.8, 141.9, 142.3, 142.8, 144.3, 145.0, 145.1, 145.4, 145.7, 145.9, 147.0, 154.6; HRMS (FAB) m/z 868.1129 (M + 1, $C_{70}H_{14}N$ requires 868.1126).

Photoreaction of C_{60} with 16. In 10% EtOH-toluene solution: 30 min irradiation, 86% conversion, column chromatography (CS_2) to yield **27** (132 mg, 55%). In 10% EtOH-ODCB solution: 30 min irradiation, 75% conversion, column chromatography (CS_2: hexane = 1:1) to yield **27** (17 mg, 7%) and **41** (101 mg, 41%).

27: ^{1}H NMR δ 2.38 (s, 3H), 2.62 (s, 3H), 4.35 (s, 2H), 4.52 (s, 2H), 6.84 (s, 1H), 7.05 (d, 2H, J = 7.8 Hz), 7.41 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 19.4, 21.1, 52.5, 58.6, 62.6, 66.5, 126.7, 129.1, 131.5, 134.4, 136.0, 136.4, 136.5, 136.8, 140.0 (2C), 141.4, 141.5, 141.7, 141.8, 142.2, 142.3 (2C), 142.8, 143.0, 144.2, 144.5, 145.1, 145.2, 145.3, 145.6, 145.9 (2C), 146.1, 146.2, 146.9, 147.0, 147.1, 154.0, 154.1; HRMS (FAB) m/z 870.1281 (M + 1, $C_{70}H_{16}N$ requires 870.1283).

41: ^{1}H NMR δ 2.37 (s, 3H), 2.65 (s, 3H), 4.2 (s, 2H), 4.39 (s, 4H), 7.02−70.6 (m, 2H), 7.42 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 19.5, 21.1, 56.9, 67.3, 70.3, 126.4, 129.3, 131.4, 132.7, 135.9, 136.8, 137.0, 139.9, 141.5, 141.7, 141.9, 142.3, 142.7, 144.2, 144.9, 145.1, 145.3, 145.7, 145.9, 146.9, 154.6; HRMS (FAB) m/z 882.1285 (M + 1, $C_{71}H_{16}N$ requires 882.1283).

Photoreaction of C_{60} with 17. In 10% EtOH-toluene solution: 20 min irradiation, 95% conversion, column chromatography (CS_2: $CHCl_3$ = 1:1) to yield **28** (176 mg, 73%). In 10% EtOH-ODCB solution: 20 min irradiation, 84% conversion, column chromatography (CS_2) to yield **28** (11 mg, 5%) and **42** (104 mg, 42%).

28: ^{1}H NMR δ 3.84 (s, 3H), 4.33 (s, 2H), 4.46 (s, 2H), 6.87 (s, 1H), 6.97 (d, 2H, J = 8.4 Hz), 7.54 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 54.0, 55.1, 58.7, 62.3, 66.6, 114.0, 129.5, 136.1, 136.5, 140.1, 140.2, 141.5 (2C), 141.7, 141.8, 141.9, 142.3, 142.4 (2C), 143.1, 144.4, 144.6, 145.2 (2C), 145.3, 145.4, 145.7, 146.0, 146.1, 146.2, 146.3, 146.6, 147.2, 154.2, 154.3, 158.8; HRMS (FAB) m/z 872.1078 (M + 1, $C_{69}H_{14}NO$ requires 872.1075).

42: ^{1}H NMR δ 3.83 (s, 3H), 4.21 (s, 2H), 4.39 (s, 4H), 6.91 (d, 2H, J = 8.7 Hz), 7.53 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 54.8, 58.0, 67.1, 70.3, 113.8, 129.5, 129.7, 136.0, 139.8, 141.5, 141.7, 141.9, 142.3, 142.8, 144.2, 144.9, 145.1, 145.3, 145.7, 145.9, 146.9, 154.6; HRMS (FAB) m/z 884.1078 (M + 1, $C_{70}H_{14}NO$ requires 884.1075).

Photoreaction of C_{60} with 18. In 10% EtOH-toluene solution: 120 min irradiation, 82% conversion, column chromatography (CS_2) to yield **29** (37 mg, 19%) and **36** (72 mg, 30%). In 10% EtOH-ODCB solution: 420 min irradiation, 89% conversion, column chromatography (CS_2) to yield **29** (44 mg, 18%), **36** (67 mg, 28%), and **43** (23 mg, 9%).

29: ^{1}H NMR δ 4.47 (s, 2H), 4.51 (s, 2H), 6.91 (s, 1H), 7.10−7.16 (m, 1H), 7.22−7.26 (m, 1H), 7.30−7.35 (m, 1H), 7.65−7.70 (m,1H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 48.1 (d, J_{C-F} = 11.7 Hz), 58.6, 62.4, 66.4, 115.4 (d, J_{C-F} = 85.8 Hz), 124.3 (d, J_{C-F} = 13.8 Hz), 126.8 (d, J_{C-F} = 58.8 Hz), 129.0 (d, J_{C-F} = 32.1 Hz), 130.4 (d, J_{C-F} = 18.3 Hz), 136.0, 136.5, 140.1 (2C), 141.5, 141.6, 141.8, 141.9, 142.2, 142.4, 142.9, 143.0, 144.3, 144.5, 145.2 (2C), 145.4, 145.6, 146.0 (2C), 146.1, 146.2, 146.5, 147.0, 147.1, 147.2, 154.0, 161.1 (d, $^1J_{C-F}$ = 980.4 Hz); HRMS (FAB) m/z 860.0873 (M + 1, $C_{68}H_{11}FN$ requires 860.0876).

36: ^{1}H NMR δ 4.87 (d, 1H, J = 10.8 Hz), 5.09 (d, 1H, J = 10.8 Hz), 6.06 (s, 1H), 7.07−7.13 (m, 1H), 7.21−7.26 (m, 1H), 7.29−7.37 (m, 1H), 7.83−7.88 (m, 1H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 61.9, 71.5, 73.0, 77.5, 115.9 (d, J_{C-F} = 87.9 Hz), 124.4 (d, J_{C-F} = 13.2 Hz), 129.5 (d, J_{C-F} = 16.2 Hz), 129.7 (d, J_{C-F} = 33.3 Hz), 135.3, 135.7, 136.3, 139.3, 139.7, 139.9 (2C), 141.3, 141.4, 141.5, 141.6, 141.7 (2C), 141.8, 141.9, 142.0, 142.1, 142.3 (2C), 142.4, 142.7, 142.8, 144.0 (2C), 144.1, 144.2, 144.8, 144.9 (2C), 145.0, 145.1, 145.2, 145.3, 145.6, 145.7 (2C), 145.9 (2C), 146.1, 146.8, 152.1, 153.2, 153.3, 155.6, 160.6 (d, $^1J_{C-F}$ = 984.6 Hz); HRMS (FAB) m/z 858.0721 (M + 1, $C_{68}H_9FN$ requires 858.0719).

43: ^{1}H NMR δ 4.37 (s, 2H), 4.45 (s, 4H), 7.11−7.17 (m, 1H), 7.27−7.29 (m, 1H), 7.32−7.37 (m, 1H), 7.79−7.84 (m, 1H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 57.8, 67.2, 70.4, 115.5 (d, J_{C-F} = 84.3 Hz), 130.3 (d, J_{C-F} = 31.5 Hz), 136.1, 139.9, 141.6, 141.8, 142.0, 142.4, 142.9, 144.3, 145.1, 145.2, 145.5, 145.8, 145.9, 146.0, 147.1, 154.8, 162.0 (d, $^1J_{C-F}$ = 974.1 Hz); HRMS (FAB) m/z 872.0880 (M + 1, $C_{69}H_{11}FN$ requires 872.0876).

Photoreaction of C_{60} with 19. In 10% EtOH-toluene solution: 120 min irradiation, 80% conversion, column chromatography (CS_2) to yield **30** (24 mg, 10%) and **37** (76 mg, 32%).

30: ^{1}H NMR δ 4.42 (s, 2H), 4.51 (s, 2H), 6.88 (s, 1H), 6.99−7.06 (m, 1H), 7.33−7.42 (m, 3H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 54.2 (d, J_{C-F} = 6.6 Hz), 58.6, 62.5, 66.4, 114.2 (d, J_{C-F} = 83.7 Hz), 115.0 (d, J_{C-F} = 84 Hz), 123.6 (d, J_{C-F} = 11.1 Hz), 130.1 (d, J_{C-F} = 31.8 Hz), 136.0, 136.5, 140.1, 140.2, 141.5 (2C), 141.6, 141.8, 141.9, 142.2, 142.4 (3C), 142.5, 143.0, 144.3, 144.5, 145.2 (d, J_{C-F} = 6 Hz), 145.3, 145.4, 145.6, 146.0 (2C), 146.1, 146.2, 146.4, 147.0 (2C), 147.2, 153.9 (d, J_{C-F} = 10.5 Hz), 163.0 (d, $^1J_{C-F}$ = 983.7 Hz); HRMS (FAB) m/z 860.0875 (M + 1, $C_{68}H_{11}FN$ requires 860.0876).

37: ^{1}H NMR δ 4.87 (d, 1H, J = 10.2 Hz), 5.09 (d, 1H, J = 10.2 Hz), 5.77 (s, 1H), 6.99−7.05 (m, 1H), 7.34−7.42 (m, 1H), 7.52−7.58 (m, 2H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 61.2, 72.0, 76.1 (d, J_{C-F} = 6.3 Hz), 76.9, 114.9 (d, J_{C-F} = 87.9 Hz), 115.2 (d, J_{C-F} = 83.7 Hz), 123.6 (d, J_{C-F} = 11.4 Hz), 130.0 (d, J_{C-F} = 32.4 Hz), 135.6, 135.8, 135.9, 136.6, 139.4, 139.7, 140.0, 140.1, 141.3, 141.5, 141.6, 141.7, 141.8, 141.9 (2C), 142.0 (2C), 142.2, 142.3, 142.4, 142.5, 142.8, 144.1, 144.4, 144.9 (2C), 145.0 (3C), 145.1 (3C), 145.3 (2C), 145.7, 145.8, 145.9, 146.0 (2C), 146.1 (2C), 146.9, 152.7, 153.4, 155.5, 162.7 (d, $^1J_{C-F}$ = 984.3 Hz); HRMS (FAB) m/z 858.0717 (M + 1, $C_{68}H_9FN$ requires 858.0719).

Photoreaction of C_{60} with 20. In 10% EtOH-toluene solution: 60 min irradiation, 79% conversion, column chromatography (CS_2: hexane = 1:1) to yield **31** (118 mg, 49%) and **38** (16 mg, 7%); 120 min irradiation, 85% conversion, column chromatography to yield **31** (44 mg, 18%) and **38** (112 mg, 47%). In 10% EtOH-ODCB solution: 120 min irradiation, 26% conversion, column chromatography (CS_2) to yield **31** (3 mg, 1%), **38** (10 mg, 4%), and **44** (26 mg, 11%); 420 min irradiation, 88% conversion, column chromatography (CS_2) to yield **31** (37 mg, 15%), **38** (60 mg, 25%), and **44** (47 mg, 19%).

31: ^{1}H NMR δ 4.40 (s, 2H), 4.50 (s, 2H), 6.88 (s, 1H), 7.12 (t, 2H, J = 8.4 Hz), 7.60−7.64 (m, 2H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 53.9, 58.6, 62.4, 66.4, 115.4 (d, J_{C-F} = 84.6 Hz), 129.7 (d, J_{C-F} = 30.9 Hz), 135.5 (d, J_{C-F} = 12 Hz), 135.9, 136.4, 140.1 (2C), 141.5 (2C), 141.6, 141.8, 141.9, 142.2, 142.4, 142.9, 143.0, 144.3, 144.5, 145.2 (2C), 145.4, 145.6, 146.0 (2C), 146.1, 146.2, 146.4, 147.0, 147.2, 153.9, 154.0, 162.0 (d, $^1J_{C-F}$ = 978.9 Hz); HRMS (FAB) m/z 860.0880 (M + 1, $C_{68}H_{11}FN$ requires 860.0876).

38: ^{1}H NMR δ 4.86 (d, 1H, J = 10.2 Hz), 5.08 (d, 1H, J = 10.2 Hz), 5.76 (s, 1H), 7.09 (t, 2H, J = 8.4 Hz), 7.76−7.81 (m, 2H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 61.4, 72.3, 76.2, 77.2, 115.6 (d, J_{C-F} = 85.5 Hz), 129.7 (d, J_{C-F} = 32.1 Hz), 133.3, 135.8, 135.9 (d, J_{C-F} = 18.9 Hz), 136.6, 139.5, 139.9, 140.1, 141.4, 141.6, 141.8, 141.9 (2C), 142.0 (2C), 142.1, 142.2 (2C), 142.4, 142.5 (2C), 142.6, 142.9, 143.1, 144.2, 144.4, 144.5, 145.1, 145.2 (2C), 145.3 (2C), 145.4, 145.6, 145.8, 145.9, 146.0 (2C), 146.1, 146.2 (2C), 146.3, 146.5, 147.1, 152.5, 153.1, 155.9, 162.6 (d, $^1J_{C-F}$ = 984 Hz); HRMS (FAB) m/z 858.0721 (M + 1, $C_{68}H_9FN$ requires 858.0719).

44: ^{1}H NMR δ 4.27 (s, 2H), 4.42 (s, 4H), 7.10−7.16 (m, 2H), 7.64−7.69 (m, 2H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 57.9, 67.3, 70.3, 115.4 (d, J_{C-F} = 84.3 Hz), 130.0 (d, J_{C-F} = 31.5 Hz), 133.4 (d, J_{C-F} = 12.6 Hz), 136.0, 139.9, 141.6, 141.8, 141.9, 142.4, 142.8, 144.3, 145.0, 145.2, 145.3, 145.7, 145.8, 146.0, 147.0, 162.0 (d, $^1J_{C-F}$ = 981.6 Hz); HRMS (FAB) m/z 872.0873 (M + 1, $C_{69}H_{11}FN$ requires 872.0876).

Photoreaction of C_{60} with 22. In 10% EtOH-toluene solution: 120 min irradiation, 65% conversion, column chromatography (CS_2) to yield **32** (45 mg, 18%) and **39** (60 mg, 24%); 300 min irradiation, 87% conversion, column chromatography to yield **32** (4 mg, 2%) and **39** (151 mg, 60%).

32: ^{1}H NMR δ 4.5 (s, 2H), 4.53 (s, 2H), 6.88 (s, 1H), 7.70 (d, 2H, J = 8.1 Hz), 7.80 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 54.1, 58.4, 62.4, 66.1, 125.4 (q, $^1J_{C-F}$ = 14.7 Hz), 128.2, 135.8, 136.3, 140.0 (2C), 141.3, 141.4, 141.6, 141.8, 142.0, 142.3 (2C), 143.6, 144.1, 144.4, 145.0, 145.1 (2C), 145.3, 145.4, 145.8, 145.9, 146.0, 146.1, 146.2, 146.8, 147.1, 153.5, 153.6; HRMS (FAB) m/z 910.0847 (M + 1, $C_{69}H_{11}F_3N$ requires 910.0844).

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39: ^{1}H NMR δ 4.9 (d, 1H, J = 9.9 Hz), 5.12 (d, 1H, J = 9.9 Hz), 5.84 (s, 1H), 7.66 (d, 2H, J = 8.4 Hz), 7.97 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 61.3, 71.8, 76.1, 76.6, 125.3 (q, $^1J_{C-F}$ = 15 Hz), 128.2, 130.3, 130.7, 135.5, 135.8 (2C), 136.7, 139.4, 139.8, 140.0, 141.3, 141.4, 141.6, 141.7, 141.8 (2C), 141.9 (2C), 142.0, 142.1, 142.3, 142.4 (2C), 142.8, 142.9, 144.0, 144.2, 144.4, 144.8, 144.9, 145.0 (2C), 145.1, 145.3 (2C), 145.4, 145.6, 145.8 (2C), 145.9, 146.0 (2C), 146.1, 146.9, 151.6, 152.5, 153.2, 155.3; HRMS (FAB) m/z 908.0690 (M + 1, $C_{69}H_9F_3N$ requires 908.0687).

Photoreactions of C_{60} with 12-C. In 10% EtOH-ODCB solution: 90 min irradiation, 44% conversion, column chromatography (CS_2) to yield **40-C** (54 mg, 23%). ^{1}H NMR δ 4.28 (d, 2H, J = 132.9 Hz), 4.42 (s, 4H), 7.33 (t, 1H, J = 7.2 Hz), 7.43 (t, 1H, J = 7.2 Hz), 7.64−7.68 (m, 2H); ^{13}C NMR ($CDCl_3$ + CS_2) δ 58.7, 67.4, 74.7, 127.5, 128.6 (d, J = 14.7 Hz), 128.7 (d, J = 11.1 Hz), 136.1, 140.0, 141.7, 141.9, 142.1, 142.5, 142.9, 144.4, 145.1, 145.3, 145.5, 145.9, 146.1, 147.1, 154.8; HRMS (FAB) m/z 855.1000 (M + 1, $C_{68}{}^{13}CH_{12}N$ requires 855.1003).

Photoreactions of C_{60} with 12-DD. In 10% EtOH-ODCB solution: 60 min irradiation, 80% conversion, column chromatography (CS_2) to yield **40-DD** (101 mg, 42%). ^{1}H NMR δ 4.43 (s, 4H), 7.34 (t, 1H, J = 7.2 Hz), 7.43 (t, 1H, J = 7.2 Hz), 7.66 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$ + CS_2) δ 67.1, 70.2, 127.4, 128.4, 135.9, 137.3, 139.8, 141.5, 141.7, 141.8, 142.2, 142.7, 144.2, 144.9, 145.1, 145.3, 145.6, 145.7, 145.8, 146.9, 154.4; HRMS (FAB) m/z 856.1092 (M + 1, $C_{69}H_{10}D_2N$ requires 856.1095).

Relative Quantum Yields of Photoreactions of C_{60} with *N*-Trimethylsilylmethyl-*N*-benzylamines. Independent N_2-purged 10% EtOH-toluene solutions (10 mL) containing the *N*-trimethylsilylmethyl-*N*-benzylamines (3.47×10^{-4} M) and C_{60} (1.74×10^{-4} M) in quartz tubes were simultaneously irradiated by using uranium glass filtered light in a merry-go-round apparatus for 5 min (<15% conversion). Each photolysate was subjected to HPLC analysis.

Cyclic Voltammetry. Cyclic voltammetry experiments were conducted using a DY2300 Electrochemical Analyzer (Digi-Ivy, TX, USA), a three-electrode one-compartment cell, an Ag/Ag^+ reference electrode (3 M $AgNO_3$), a coiled platinum counter electrode, and glassy carbon electrode (2 mm diameter). The potential range used in the cyclic voltammetric measurements was between −1.2 and +3.0 V (vs Ag/Ag^+) with a scan rate of 0.05 V/s. Then, the potential values were calibrated against the oxidation potential of 1 mM ferrocene (vs Ag/Ag^+) as a standard (E^o (Fc^+/Fc) = 0.09 V vs Ag/Ag^+).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00004.

^{1}H and ^{13}C NMR spectra of all previously unidentified compounds, UV−visible spectra, and cyclic voltamograms of new substances (PDF)

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Notes

The authors declare no competing financial interest.

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