

HETEROCYCLES, Vol. 93, No. 1, 2016, pp. 202 - 217. © 2016 The Japan Institute of Heterocyclic Chemistry
Received, 24th August, 2015, Accepted, 17th September, 2015, Published online, 7th October, 2015
DOI: 10.3987/COM-15-S(T)19

SYNTHESIS OF FUNCTIONALIZED FULLERENES BY PHOTOADDITION OF *N*- α -TRIMETHYLSILYL-*N*-CARBOXYMETHYL-*N*-BENZYLAMINES TO C₆₀

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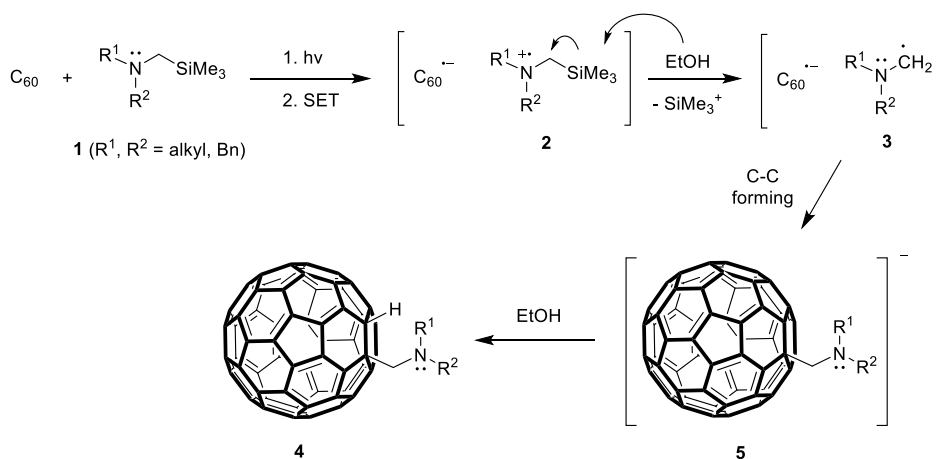
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Abstract – Photoaddition reactions of fullerene C₆₀ with *N*- α -trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines, which contain various para-substituents, were explored in order to evaluate factors governing efficiencies of this potentially useful method for preparing functionalized fullerene derivatives. Observations made in this study show that two reaction pathways are followed in these photoreactions. The first involves initial formation of α -trimethylsilyl-aminium radicals and the C₆₀ anion radical by SET from the amines to the triplet excited state of C₆₀. This step is followed by desilylation to produce α -amino radicals. Coupling of these radicals with the anion radical of C₆₀ followed by protonation or with the hydrofullerene radical generated by protonation of the anion radical of C₆₀ then produces aminomethyl-1,2-dihydrofullerenes. When limited amounts of ³O₂ are present in the reaction medium, fulleropyrrolidines are generated in low yields by a competitive pathway involving formation of singlet oxygen, which undergoes sequential H-atom abstractions from the *N*- α -trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines to produce azomethine ylide intermediates. Dipolar cycloaddition of the ylides to C₆₀ then produces fulleropyrrolidines. Photoreactions of the C₆₀ and the amines in the presence of high ³O₂ concentrations exclusively produce fulleropyrrolidine. In addition, the results show that photoreactions of non-silicon substituted, *N*-methyl-*N*-carboxymethyl-*N*-benzylamines with C₆₀ form fulleropyrrolidines

independent of the concentration of $^3\text{O}_2$ present in the media.

INTRODUCTION

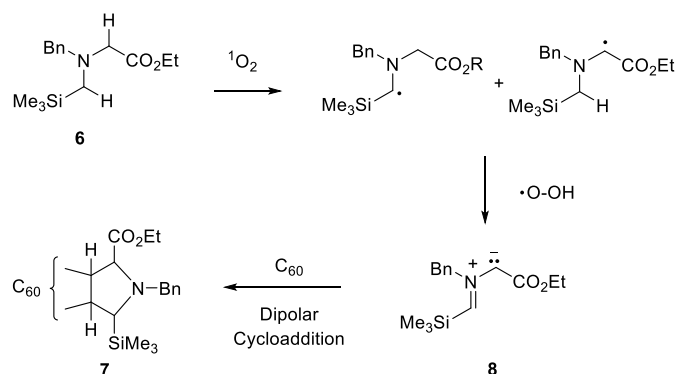
Thermal and photochemical reactions of fullerenes have been broadly explored in order to develop methods to prepare novel substituted fullerenes that can potentially serve as unique electron accepting materials.¹⁻⁶ The most common approaches employed for the preparation of these substances involve 1,3-dipolar cycloaddition,⁷⁻⁹ cyclopropanation^{10,11} and radical coupling reactions.^{12,13} In addition, single electron transfer (SET) promoted photochemical reactions between fullerene and electron donating substances¹⁴⁻¹⁷ also serve as useful methods for synthesizing substituted fullerenes. These reactions are driven by the high electron affinities¹⁸ and relatively high reduction potential ($^3E_{\text{red}}(\text{C}_{60}) = 1.14 \text{ V vs SCE}$)¹⁹ of the triplet excited state of C_{60} . Observations made in earlier studies¹⁷ show that SET promoted photoaddition reactions take place between tertiary amines and fullerene to produce aminomethyl substituted 1,2-dihydrofullerene derivatives. Moreover, when α -trimethylsilyl substituted tertiary amines (**1**, Scheme 1) are used as electron donor substrates, photoaddition reactions with C_{60} generate aminomethyl-1,2-dihydrofullerenes **4** in a highly efficient manner. The mechanistic pathway operating in these photoaddition reactions involves initial SET from the amine to the excited state of fullerene to form the corresponding amine radical cations **2** (*i.e.*, aminium radicals) and fullerene radical anion. Subsequent desilylation of the formed aminium radical occurs to produce an α -amino radical **3** that couples with the fullerene radical anion (or the corresponding protonated hydrofullerenyl radical) to generate the anion precursor **5** of the fullerene-adduct (or directly the fullerene-adduct).



Scheme 1

Recently, we observed that the efficiencies of photoaddition reactions of amines with C_{60} are highly dependent on the electronic nature of the amine substrates.¹⁷ For instance, photoreactions of deoxygenated 10% EtOH-toluene solutions containing C_{60} and *N*- α -trimethylsilyl-*N,N*-dibenzylamines

that contains electron donating substituents (*e.g.*, Me, OMe) on the phenyl rings, take place efficiently to form the corresponding aminomethyl substituted 1,2-dihydrofullerene adducts in modestly high yields. In contrast, photoreactions of *N*- α -trimethylsilyl-*N,N*-dibenzylamines, which contain electron withdrawing phenyl substituents (*i.e.*, F, CF₃), require longer irradiation times and produce 1,2-adducts in low yields.^{17b} In addition, photoreactions of deoxygenated solutions of C₆₀ and benzylamines, which contain electron withdrawing *N*-carboxymethyl groups (*e.g.* **6** in Scheme 2), not only require longer irradiation times and they produce either low yields of aminomethyl-1,2-dihydrofullerene adducts (under N₂ purged 10% EtOH-toluene) or fulleropyrrolidines (*e.g.* **7** in Scheme 2) exclusively (oxygenated 10% EtOH-toluene).^{17a} These results show that photoreactions of *N*-carboxymethyl substituted amines in the presence of molecular oxygen take place via a pathway that involves singlet molecular oxygen (¹O₂) mediated generation of azomethine ylides (*e.g.* **8** in Scheme 2), reactive intermediates that undergo 1,3-dipolar cycloadditions to fullerene.^{7-9,17}



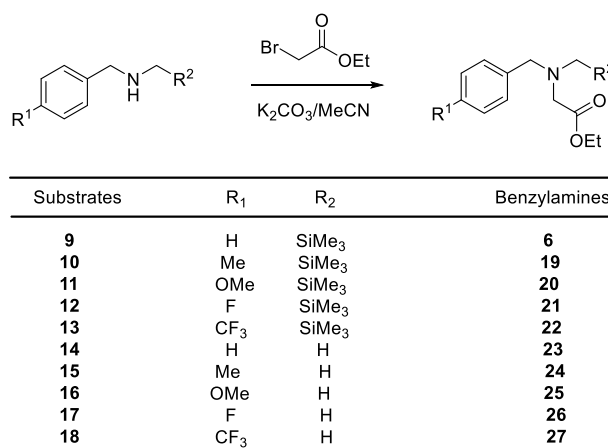
Scheme 2

The unique effects of *N*-carboxymethyl substituents on the nature of photochemical reactions of amines with C₆₀ and substituent effects on efficiencies of SET promoted photochemical reactions of C₆₀ with tertiary *N*- α -trimethylsilyl-*N*-benzylamines are interesting in that they help guide the design of methods to prepare variously functionalized fullerenes. To gain more information about the preparative utility of these processes, an investigation was designed to explore photochemical reactions of fullerene C₆₀ with electron donating and withdrawing *para*-phenyl substituted *N*-carboxymethyl-*N*- α -trimethylsilyl-*N*-benzylamines and analogs not containing trimethylsilyl groups. The major goal of this effort was to elucidate if and how the electronic nature of the amine substituents, the presence of α -trimethylsilyl groups and photoreaction conditions affect the efficiencies and nature of these processes. Observation made in this study, summarized below, show that two competitive photochemical pathways are followed in these systems, one involving formation of aminium radicals by SET from the amine to the triplet excited state of C₆₀ followed by desilylation leading to formation of aminomethyl-1,2-dihydrofullerenes and the other involving formation of azomethine ylides by singlet

oxygen mediated H-atom abstraction from amine followed by cycloaddition to lead to formation of fulleropyrrolidine adducts. The relative importance of these pathways depends on both the nature of phenyl ring substituents, the presence or absence of α -trimethylsilyl groups and high concentrations of $^3\text{O}_2$.

RESULTS AND DISCUSSION

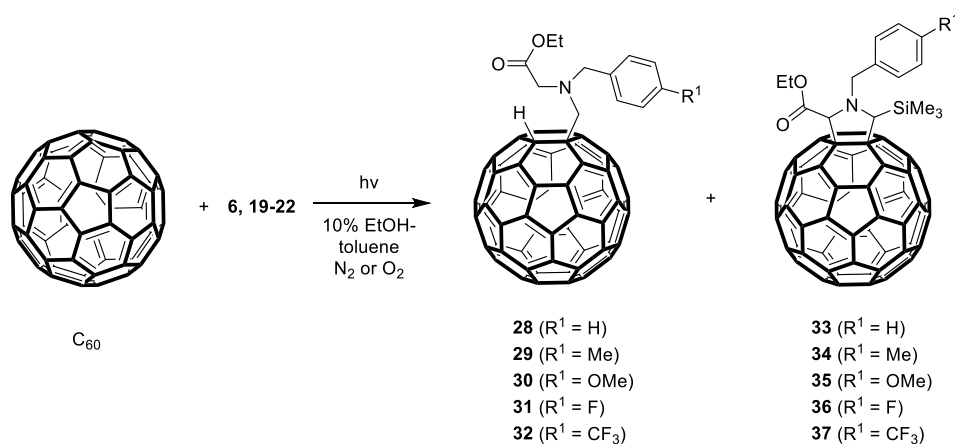
Synthesis of N - α -trimethylsilyl- N -carboxymethyl- N -benzylamines. The N - α -trimethylsilyl- N -carboxymethyl- N -benzylamines, **6** and **19-22**, utilized in this study were readily prepared by using substitution reactions between available N - α -trimethylsilyl- N -benzylamines **9-13** and ethyl bromoacetate in the presence of K_2CO_3 in MeCN (Scheme 3). In addition, in order to elucidate the effect of trimethylsilyl groups on these photoreactions, non-trimethylsilyl containing benzylamine analogs, **23-27**, were also prepared using similar processes (Scheme 3).



Scheme 3

Photoreactions of C_{60} with N - α -trimethylsilyl- N -carboxymethyl- N -benzylamines and non-trimethylsilyl containing counterparts. The yields and product distributions of photoreactions of C_{60} with the silyl/non-silyl benzylamines **6** and **19-22**, which have various substituents at *para* position of the phenyl rings, were determined. All photochemical reactions were carried out by irradiating (450 W Hanovia medium pressure mercury lamp and flint glass filter $\lambda > 300$ nm) 10% EtOH-toluene solutions containing C_{60} (0.28 mmol) and benzylamines (0.59 mmol). The photolysates were triturated with CHCl_3 to recover C_{60} and the triturates were concentrated in vacuo to generate residues, which were subjected to silica gel column chromatography to obtain pure photoproducts. Structural assignments to the photoproducts were made based on analysis of ^1H and ^{13}C NMR, and UV-visible spectra, and by using HRMS (see Experimental and Supporting data), as well as by comparing the data to those previously reported^{17a} for related compounds.

The results show that photoreactions of C_{60} with α -trimethylsilyl containing benzylamines **6**, and **19-22**, carried out on N_2 purged solutions, generate two types of photoproducts, including aminomethyl-1,2-dihydrofullerenes **28-32** and fulleropyrrolidines **33-37** (Scheme 4 and Table 1). Specifically, 1 h irradiation of solutions of C_{60} and amines **19** and **20** (0.59 mmol) possessing electron donating substituted (Me and OMe) phenyl rings as well as the unsubstituted analog **6**, brings about high conversion of C_{60} and modestly high yielding formation of the corresponding aminomethyl-1,2-dihydrofullerenes **28-30** predominantly, along with low yielding generation of fulleropyrrolidines **33-35** (Table 1, entries 1-3). In contrast, photoreactions of C_{60} with electron withdrawing group (F and CF_3) substituted benzylamines **21** and **22** (entries 4-5, Table 1) require longer irradiation times to bring about high C_{60} conversions. Significantly, these reactions occur in lower yields and they generate fulleropyrrolidines **36** and **37** in relatively larger amounts. Furthermore, the results of previous studies,^{17a} showing that aminomethyl-1,2-dihydrofullerene **28**^{17a} is not converted to fulleropyrrolidine **33**^{17a} upon prolonged photoirradiation, demonstrate that two types of adducts formed in these photoreactions arise by independent pathways.



Scheme 4

Table 1. Products and yields of photoaddition reactions of N_2 purged 10% EtOH-toluene solutions containing C_{60} and **6** and **19-22**.

Entry	Amine	Irradiation Time (h)	Conversion (%) ^b	Product (%) ^c
1	6	1	95	28 (68), 33 (10)
2	19	1	100	29 (69), 34 (2)
3	20	1	100	30 (70), 35 (3)
4	21	3	89	31 (57), 36 (10)
5	22	3	77	32 (40), 37 (10)

6 ^d	6	1	100	28 (76), 33 (12)
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^a α -Silylamines (0.56 mmol) and C₆₀ (0.28 mmol) in 220 mL of 10% EtOH-toluene.
^bConversions determined based on recovered C₆₀. ^cYields of isolated products. ^dPrevious result (ref. 17a)

We postulated that the small yet finite amounts of O₂, which are present in photoreaction mixtures that are purged with nitrogen, are responsible for formation of the fulleropyrrolidine adducts (see below). In order to explore this proposal, photoreaction of C₆₀ with α -trimethylsilyl benzylamine **6** was carried out using a completely deoxygenated solution (by using a freeze-pump-thaw method). Specifically, a 10% EtOH-toluene solution (7 mL) containing C₆₀ (1.74 x 10⁻⁴ M) and benzylamine **6** (3.46 x 10⁻⁴ M) was added to Schlenk flask and then subjected to a repetitive freeze-pump-thaw degassing process to remove O₂ completely. Irradiation of this solution under a N₂ atmosphere was carried out for 2.5 h and the photolysate was analyzed by using HPLC. Importantly, analysis of chromatogram showed that the aminomethyl-1,2-difullerene adduct **28** (retention time 6.3 min) is produced exclusively and that none of the fulleropyrrolidine **33** is formed (retention time 11.9 min) (See Supporting Data).

The effect of molecular oxygen on these processes was explored next. The results show that irradiation of oxygenated 10% EtOH-toluene solutions containing C₆₀ and benzylamines **6**, **19-22** under the same conditions as described above leads to exclusive formation of the corresponding fulleropyrrolidines **33-37** in modestly high yields (Table 2). Longer irradiation times are required for these photoreactions regardless of the nature of the benzylamine substituent.

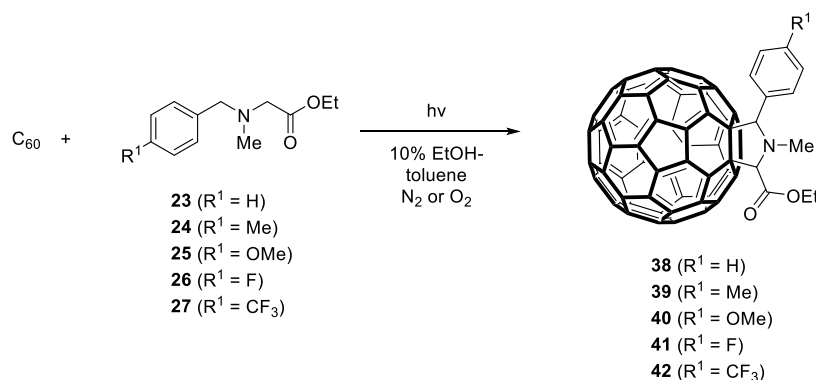
Table 2. Products and yields of photoaddition reactions of O₂ purged 10% EtOH-toluene solutions containing C₆₀ and **6** and **19-22**.

Entry	Amine	Irradiation Time (h)	Conversion (%) ^b	Product (%) ^c
1	6	2	89	33 (57)
2	19	2	90	34 (56)
3	20	2	90	35 (57)
4	21	2	68	36 (41)
5	21	4	85	36 (56)
6	22	2	56	37 (32)
7	22	4	81	37 (51)
8 ^d	6	2	91	38 (70)

^a α -Silylamines (0.56 mmol) and C₆₀ (0.28 mmol) in 220 mL of 10% EtOH-toluene.

^bConversions determined based on recovered C₆₀. ^cYields of isolated products. ^dPrevious result (ref. 17a)

To investigate the effect of the trimethylsilyl group in the amine substrates on the nature and efficiencies of the photoreaction, nitrogen or oxygen purged 10% EtOH-toluene solutions of C_{60} and the non-trimethylsilyl containing benzylamines **23-27** were irradiated. The results (Scheme 5 and Tables 3 and 4) show that these photoreactions, taking place under both conditions, require longer irradiation times and yield fulleropyrrolidine adducts **38-42** exclusively.



Scheme 5

Table 3. Products and yields of photoaddition reactions of N_2 purged 10% EtOH-toluene solutions containing C_{60} and **23-27**.

Entry	Amine	Irradiation Time (h)	Conversion (%) ^b	Product (%) ^c
1	23	2	59	38 (37)
2	24	2	60	39 (35)
3	25	2	60	40 (38)
4	26	5	76	41 (40)
5	27	5	72	42 (42)
6 ^d	23	2	55	38 (30)

^aAmines (0.56 mmol) and C_{60} (0.28 mmol) in 220 mL of 10% EtOH-toluene.

^bConversions determined based on recovered C_{60} . ^cYields of isolated products. ^dPrevious result (ref. 17a)

Table 4. Products and yields of photoaddition reactions of O_2 purged 10% EtOH-toluene solutions containing C_{60} and **23-27**.

Entry	Amine	Irradiation Time (h)	Conversion (%) ^b	Product (%) ^c
1	23	5	66	38 (35)
2	24	5	67	39 (35)

3	25	5	70	40 (42)
4	26	5	60	41 (32)
5	27	5	57	42 (32)
6	27	8	85	42 (50)

^aAmines (0.56 mmol) and C₆₀ (0.28 mmol) in 220 mL of 10% EtOH-toluene.

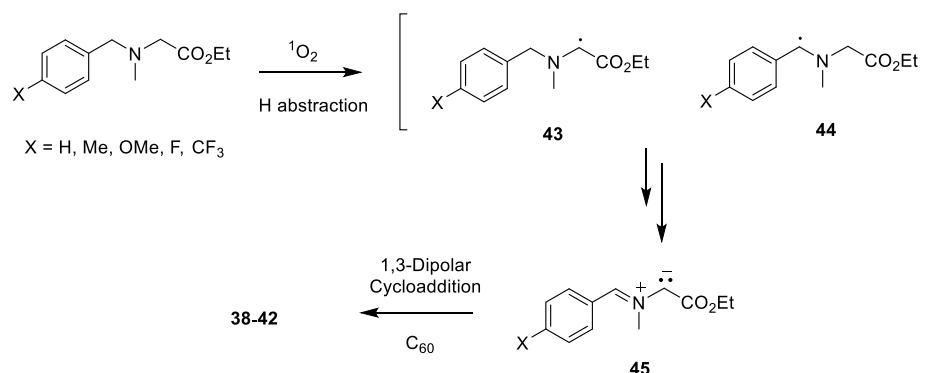
^bConversions determined based on recovered C₆₀. ^cYields of isolated products.

Effect of amine substituents and structures on photoaddition reaction efficiencies. As can be seen from viewing the data given in Tables 1 and 2, the electronic nature of the *p*-phenyl substituent in *N*- α -trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines plays a surprisingly important role in governing efficiencies of photoaddition reactions with C₆₀. The results show that photoaddition reactions of non- and electron-donating group substituted amine substrates take place more efficiently than those of the electron withdrawing group substituted analogs. Moreover, it is clear that two independent processes occur when solutions of C₆₀ and the amines are irradiated. One produces aminomethyl-1,2-dihydrofullerenes **28-32** and the other fulleropyrrolidines **33-37**. Consequently, two competing, mechanistically different pathways are followed in these reactions. The route leading to 1,2-dihydrofullerenes **28-32** is almost certainly initiated by SET from the amines to the triplet excited state of C₆₀, produced by direct excitation followed by rapid intersystem crossing.²⁰ Because the rates of SET from all benzylamines to the triplet excited state of C₆₀ are predicted to be near equal to that of diffusion control,^{17a,19} differences in the efficiencies of 1,2-dihydrofullerene formation need to be associated with the rates of EtOH promoted desilylation of intermediate aminium radicals which competes with energy wasting/efficiency diminishing back SET from the aminium radicals to the anion radical of C₆₀. Alternatively, the substituents could influence the rates of α -amino radical coupling with the anion radical of C₆₀ or its protonated conjugate acid. Frankly, as discussed earlier,^{17b} both of these possibilities are difficult to understand because of the remoteness of the location of the substituents relative to the centers participating in aminium radical desilylation and amino radical coupling.

In contrast, the pathway followed in fulleropyrrolidine forming photoreactions of *N*- α -trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines is more firmly understood. Specifically, this process takes place via a route that involves singlet oxygen mediated formation of azomethine ylides that then undergo familiar⁷⁻⁹ dipolar cycloadditions to C₆₀ (Scheme 2). As suggested by Foote^{20a} earlier, the triplet excited state of C₆₀ should undergo energy transfer to ³O₂ to form ¹O₂ and ground-state C₆₀, a process that competes with or dominates over SET from the amine depending upon on the concentration of ³O₂. In the manner described by Foote,^{20a} ¹O₂ then reacts with the *N*-carboxymethyl-*N*- α -trimethylsilyl-*N*-benzylamine through

sequential α -hydrogen atom abstractions to form the key azomethine ylide (Scheme 2). This proposal is helpful in explaining why fulleropyrrolidines are formed in increased amounts relative to the aminomethyl-1,2-dihydrofullerenes in photoreactions of electron withdrawing group substituted substrates in deoxygenated solutions. In these cases, $^1\text{O}_2$ is produced from small amounts of $^3\text{O}_2$ present under these conditions. Owing to the fact that aminomethyl-1,2-dihydrofullerene production is highly inefficient in these cases, fulleropyrrolidine formation would become more competitive.

Another observation made in this effort has both preparative and mechanistic significance. As can be seen from viewing the data in Tables 3 and 4, photoreactions of C_{60} with non-trimethylsilyl substituted benzylamines require much longer irradiation times to bring about high conversions of C_{60} . In addition, these processes generate fulleropyrrolidines **38-42** exclusively. Of equal interest is the structural nature of generated fulleropyrrolidines. As discussed above, azomethine ylide intermediates formed in photoreactions of the *N*- α -trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines involving the intermediacy of $^1\text{O}_2$ arise by H-atom abstractions pathways. The nature of the cycloadducts dictates that loss of hydrogens in these processes takes place exclusively from the trimethylsilyl and alkoxy carbonyl substituted α -carbons and not the benzylic position of the amines (see Scheme 2). However, in $^1\text{O}_2$ promoted reactions of the non-trimethylsilyl substituted amines H-atom abstractions occurs at the amine alkoxy carbonyl and aryl substituted α -centers exclusively to generate α -amino radicals **43** and **44** and, eventually, azomethine ylide **45** (Scheme 6).



Scheme 6

In this study, photochemical reactions of fullerene C_{60} with *N*- α -trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines that contain various substituents at *para* position on the phenyl ring were carried out. Observation made in this study show that two competitive photochemical pathways are followed in these reactions, one involving formation of aminium radicals by SET from the amine to the triplet excited state of C_{60} followed by desilylation leading to formation of aminomethyl-1,2-dihydrofullerenes and the other involving formation of azomethine ylides by singlet oxygen mediated H-atom abstraction from amine followed by cycloaddition to form fulleropyrrolidines.

The relative importance of these pathways depends on both the nature of phenyl ring substituents, the presence or absence of α -trimethylsilyl groups and the concentration of $^3\text{O}_2$.

EXPERIMENTAL

General Procedure ^1H and ^{13}C NMR spectra were recorded on CDCl_3 solutions and chemical shifts are reported in parts per million relative to CHCl_3 (7.24 ppm for ^1H and 77.0 ppm for ^{13}C) 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 starting materials used in the photoreactions derived from commercial sources. All new compounds described were isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

***N*- α -Trimethylsilyl-*N*-carboxymethyl-*N*-benzylamines 19-22.** Individual solutions of *N*- α -trimethylsilyl-*N*-benzylamines **10-13** (2.0 g, 9.6 mmol of **10**, 2.0 g, 9 mmol of **11**, 2.1 g, 9.9 mmol of **12**, and 1.5 g, 5.7 mmol of **13**) in MeON (100 mL) containing K_2CO_3 (2.7 g, 19 mmol) and ethyl bromoacetate (1.8 g for **10**, 2.5 g for **11**, 4.3 g for **12**, and 1.2 g for **13**) were stirred for 12 h at room temperature and concentrated in vacuo to give residues which were triturated with CH_2Cl_2 . The triturates were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc: hexane = 1: 20) to yield **19** (1.5 g, 53%), **20** (1.9 g, 70%), **21** (2.6 g, 88%), and **22** (1.2 g, 56%).

19: ^1H -NMR 0.06 (s, 9H), 1.25 (t, 3H, $J = 7.2$ Hz), 2.20 (s, 2H), 2.31 (s, 3H), 3.23 (s, 2H), 3.72 (s, 2H), 4.13 (q, 2H, $J = 7.2$ Hz), 7.09 (d, 2H, $J = 7.8$ Hz), 7.22 (d, 2H, $J = 7.8$ Hz); ^{13}C -NMR -1.7, 14.0, 20.8, 45.3, 56.4, 59.7, 60.8, 128.6, 129.5, 135.6, 136.3, 170.8; HRMS (EI) m/z 293.1812 (M, $\text{C}_{16}\text{H}_{27}\text{NO}_2\text{Si}$ requires 293.1811).

20: ^1H -NMR 0.05 (s, 9H), 1.24 (t, 3H, $J = 7.2$ Hz), 2.17 (s, 2H), 3.21 (s, 2H), 3.67 (s, 2H), 3.77 (s, 3H), 4.12 (q, 2H, $J = 7.2$ Hz), 6.82 (d, 2H, $J = 8.7$ Hz), 7.24 (d, 2H, $J = 8.7$ Hz); ^{13}C -NMR -1.5, 14.3, 45.5, 55.1, 56.8, 59.9, 60.7, 113.5, 129.9, 131.4, 158.6, 171.4; HRMS (EI) m/z 309.1757 (M, $\text{C}_{16}\text{H}_{27}\text{NO}_3\text{Si}$ requires 309.1760).

21: ^1H -NMR 0.03 (s, 9H), 1.24 (t, 3H, $J = 7.2$ Hz), 2.15 (s, 2H), 3.22 (s, 2H), 3.69 (s, 2H), 4.12 (q, 2H, $J = 7.2$ Hz), 6.97 (t, 2H, $J = 8.7$ Hz), 7.26-7.31 (m, 2H); ^{13}C -NMR -1.7, 14.1, 45.3, 56.8, 59.8, 60.6, 114.8 (d, $J = 83.7$ Hz), 130.1 (d, $J = 31.5$ Hz), 135.1 (d, $J = 12$ Hz), 161.8 (d, $J = 972.3$ Hz), 171.7; HRMS (EI) m/z 297.1562 (M, $\text{C}_{15}\text{H}_{24}\text{FNO}_2\text{Si}$ requires 297.1560).

22: ^1H -NMR 0.04 (s, 9H), 1.25 (t, 3H, $J = 7.2$ Hz), 2.19 (s, 2H), 3.26 (s, 2H), 3.82 (s, 2H), 4.14 (q, 2H, $J = 7.2$ Hz), 7.46 (d, 2H, $J = 8.1$ Hz), 7.54 (d, 2H, $J = 8.1$ Hz); ^{13}C -NMR -1.7, 14.2, 45.5, 56.9, 60.1, 61.1, 125.1 (q, $J = 14.7$ Hz), 128.8, 143.7, 171.0; HRMS (EI) m/z 347.1527 (M, $\text{C}_{16}\text{H}_{24}\text{F}_3\text{NO}_2\text{Si}$ requires 347.1528).

Photoreactions of C₆₀ with Amines. Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a glass filter (>300 nm) in a water-cooled quartz immersion well surrounded by the solution being irradiated, consisting of 10% EtOH-toluene solution (220 mL) containing C₆₀ (0.28 mmol) and the amine (0.56 mmol). The solution being irradiated was purged with either nitrogen or oxygen before and during irradiations for the time periods given below. The photolysates were triturated with CHCl₃ to recover C₆₀ and the triturates were concentrated in vacuo to generate residues, which were subjected to silica gel column chromatography to generate the pure photoproducts.

Photoreaction of C₆₀ with Amine 6. Formation of 28 and 33. N₂ saturated condition. 1 h irradiation, 95% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **28** (175 mg, 68%) and **33** (27 mg, 10%). O₂ saturated condition. 2 h irradiation, 88% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **33** (157 mg, 57%).

Photoreaction of C₆₀+19. Formation of 29 and 34. N₂ saturated condition. 1 h irradiation, 100% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **29** (179 mg, 69%) and **34** (7 mg, 2%). O₂ saturated condition. 2 h irradiation, 90% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **34** (158 mg, 56%).

29: ¹H-NMR 1.35 (t, 3H, *J* = 7.2 Hz), 2.36 (s, 3H), 3.90 (s, 2H), 4.28 (q, 2H, *J* = 7.2 Hz), 4.48 (s, 2H), 4.74 (s, 2H), 6.99 (s, 1H), 7.17 (d, 2H, *J* = 7.8 Hz), 7.48 (d, 2H, *J* = 7.8 Hz); ¹³C-NMR (CDCl₃+CS₂) 14.4, 21.2, 55.3, 57.9, 59.4, 60.4, 67.1, 68.2, 129.1, 129.2, 135.0, 135.8, 135.9, 137.0, 139.9, 140.1, 141.4 (2C), 141.6, 141.7, 141.8, 142.1, 142.3 (2C), 143.0, 144.3, 144.5, 145.1 (3C), 145.2, 145.6, 145.9 (2C), 146.1 (2C), 146.5, 147.0 (2C), 147.1, 154.3, 154.6, 170.7; HRMS (FAB) *m/z* 942.1491 (M+1, C₇₃H₂₀NO₂ requires 942.1494).

34: ¹H-NMR 0.51 (s, 9H), 1.17 (t, 3H, *J* = 7.2 Hz), 2.40 (s, 3H), 4.17 (q, 1H, *J* = 7.2 Hz), 4.28 (q, 1H, *J* = 7.2 Hz), 4.53 (d, 1H, *J* = 13.2 Hz), 5.30 (d, 1H, *J* = 13.2 Hz), 5.37 (s, 1H), 5.43 (s, 1H), 7.23 (d, 2H, *J* = 7.8 Hz), 7.50 (d, 2H, *J* = 7.8 Hz); ¹³C-NMR (CDCl₃+CS₂) 0.7, 14.1, 21.2, 55.7, 60.6, 69.8, 76.2, 77.2, 77.8, 128.5, 129.4, 134.7, 135.5, 135.6, 135.7, 136.0, 137.1, 139.1, 139.3, 139.4, 140.0, 141.5, 141.6, 141.7, 141.8, 141.9, 142.0 (3C), 142.1 (2C), 142.3, 142.5 (3C), 142.6, 142.9, 143.0, 144.1, 144.2, 144.3, 144.4, 144.9 (2C), 145.0 (2C), 145.1 (3C), 145.3, 145.4, 145.7, 145.8 (2C), 145.9 (2C), 146.0, 146.1, 146.2, 146.5, 146.8 (2C), 152.6, 154.8, 156.4, 157.1, 170.2; HRMS (FAB) *m/z* 1012.1729 (M+1, C₇₆H₂₆NO₂Si requires 1012.1733).

Photoreaction of C₆₀+20. Formation of 30 and 35. N₂ saturated condition. 1 h irradiation, 100% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **30** (186 mg, 70%) and **35** (8 mg, 3%). O₂ saturated condition. 2 h irradiation, 90% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **35** (163 mg, 57%).

30: $^1\text{H-NMR}$ 1.36 (t, 3H, $J = 6.9$ Hz), 3.80 (s, 3H), 3.90 (s, 2H), 4.29 (q, 2H, $J = 6.9$ Hz), 4.46 (s, 2H), 4.74 (s, 2H), 6.90 (d, 2H, $J = 8.1$ Hz), 6.97 (s, 1H), 7.50 (d, 2H, $J = 8.1$ Hz); $^{13}\text{C-NMR}$ ($\text{CDCl}_3 + \text{CS}_2$) 14.4, 55.0, 55.5, 58.0, 59.1, 60.5, 67.3, 68.2, 113.9, 130.1, 130.4, 135.9, 136.0, 139.9, 140.1, 141.5 (2C), 141.7, 141.8, 141.9, 142.2, 142.4 (2C), 143.1, 144.4, 145.2 (3C), 145.3, 145.7, 146.0 (2C), 146.2 (2C), 146.7, 147.1 (2C), 147.2, 154.3, 154.7, 159.0, 171.1; HRMS (FAB) m/z 958.1447 (M+1, $\text{C}_{73}\text{H}_{20}\text{NO}_3$ requires 958.1443).

35: $^1\text{H-NMR}$ 0.50 (s, 9H), 1.16 (t, 3H, $J = 7.2$ Hz), 3.84 (s, 3H), 4.19 (q, 1H, $J = 7.2$ Hz), 4.29 (q, 1H, $J = 7.2$ Hz), 4.50 (d, 1H, $J = 12.9$ Hz), 5.19 (d, 1H, $J = 12.9$ Hz), 5.36 (s, 1H), 5.44 (s, 1H), 6.96 (d, 2H, $J = 8.7$ Hz), 7.53 (d, 2H, $J = 8.7$ Hz); $^{13}\text{C-NMR}$ ($\text{CDCl}_3 + \text{CS}_2$) 0.7, 14.1, 55.0, 55.4, 60.7, 69.8, 76.1, 77.5, 77.8, 114.1, 129.7, 130.7, 134.8, 135.5, 135.6, 136.0, 139.1, 139.3, 139.5, 140.1, 141.6 (2C), 141.7, 141.8, 141.9, 142.0 (2C), 142.1 (2C), 142.2, 142.3, 142.5 (2C), 142.6 (2C), 142.9, 143.0, 144.1, 144.3 (2C), 144.4, 144.9, 145.0 (2C), 145.1 (3C), 145.4, 145.7, 145.8 (2C), 145.9, 146.0 (2C), 146.1, 146.3, 146.5, 146.8, 146.9, 152.7, 154.9, 156.4, 157.2, 159.1, 170.3; HRMS (FAB) m/z 1028.1685 (M+1, $\text{C}_{76}\text{H}_{26}\text{NO}_3\text{Si}$ requires 1028.1682).

Photoreaction of $\text{C}_{60} + \mathbf{21}$. Formation of $\mathbf{31}$ and $\mathbf{36}$. N_2 saturated condition. 3 h irradiation, 89% conversion, column chromatography (CS_2 : hexane = 1: 1) to yield **31** (151 mg, 57%) and **36** (29 mg, 10%). O_2 saturated condition. 2 h irradiation, 68% conversion, column chromatography (CS_2 : hexane = 1: 1) to yield **36** (116 mg, 41%); 4 h irradiation, 85% conversion, column chromatography (CS_2 : hexane = 1: 1) to yield **36** (147 mg, 56%).

31: $^1\text{H-NMR}$ 1.37 (t, 3H, $J = 7.2$ Hz), 3.89 (s, 2H), 4.29 (q, 2H, $J = 7.2$ Hz), 4.50 (s, 2H), 4.75 (s, 2H), 6.96 (s, 1H), 7.05 (t, 2H, $J = 8.4$ Hz), 7.57 (t, 2H, $J = 8.4$ Hz); $^{13}\text{C-NMR}$ ($\text{CDCl}_3 + \text{CS}_2$) 14.3, 55.2, 57.8, 58.8, 60.5, 67.0, 68.3, 115.3 (d, $J = 84$ Hz), 130.6 (d, $J = 30.9$ Hz), 133.7 (d, $J = 12.9$ Hz), 135.8 (d, $J = 18$ Hz), 139.8, 140.1, 141.4 (2C), 141.5, 141.7, 141.8, 142.0, 142.3 (2C), 143.0, 144.2, 144.4, 145.1, 145.2, 145.5, 145.9 (2C), 146.1 (2C), 146.4, 146.9, 147.1, 154.0, 154.3, 162.0 (d, $J = 982.2$ Hz), 170.4; HRMS (FAB) m/z 946.1245 (M+1, $\text{C}_{72}\text{H}_{17}\text{NO}_2\text{F}$ requires 946.1243).

36: $^1\text{H-NMR}$ 0.51 (s, 9H), 1.18 (t, 3H, $J = 7.2$ Hz), 4.20 (q, 1H, $J = 7.2$ Hz), 4.27 (q, 1H, $J = 7.2$ Hz), 4.55 (d, 1H, $J = 13.2$ Hz), 5.23 (d, 1H, $J = 13.2$ Hz), 5.37 (s, 1H), 5.40 (s, 1H), 7.13 (t, 2H, $J = 8.7$ Hz), 7.58-7.63 (m, 2H); $^{13}\text{C-NMR}$ ($\text{CDCl}_3 + \text{CS}_2$) 0.6, 14.1, 55.2, 60.6, 69.6, 76.1, 77.3, 77.6, 115.5 (d, $J = 84.9$ Hz), 129.9 (d, $J = 31.2$ Hz), 134.3 (d, $J = 12$ Hz), 134.6, 135.4 (2C), 136.0, 139.1, 139.3, 139.4, 140.0, 141.5 (2C), 141.6 (2C), 141.7, 141.8, 141.9 (2C), 142.0 (2C), 142.2, 142.4 (2C), 142.5 (2C), 142.8, 142.9, 144.0, 144.1, 144.2, 144.3, 144.7, 144.9 (2C), 145.0 (4C), 145.2, 145.6, 145.7, 145.9 (2C), 146.0, 146.1, 146.3, 146.7, 146.8, 152.4, 154.5, 156.1, 156.9, 162.1 (d, $J = 980.1$ Hz), 169.8; HRMS (FAB) m/z 1016.1485 (M+1, $\text{C}_{75}\text{H}_{23}\text{FNO}_2\text{Si}$ requires 1016.1482).

Photoreaction of C₆₀+22. Formation of 32 and 37. N₂ saturated condition. 3 h irradiation, 77% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **32** (112 mg, 40%) and **37** (30 mg, 10%). O₂ saturated condition. 2 h irradiation, 56% conversion, column chromatography (CS₂:hexane = 1: 1) to yield **37** (96 mg, 32%); 4 h irradiation, 81% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **37** (141 mg, 51%).

32: ¹H-NMR 1.37 (t, 3H, *J* = 7.2 Hz), 3.89 (s, 2H), 4.30 (q, 2H, *J* = 7.2 Hz), 4.63 (s, 2H), 4.79 (s, 2H), 6.99 (s, 1H), 7.63 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.1 Hz); ¹³C-NMR (CDCl₃+CS₂) 14.3, 55.5, 57.9, 59.1, 60.7, 67.0, 68.7, 125.5 (d, *J* = 14.7 Hz), 129.2, 135.8, 135.9, 139.9, 140.2, 141.4, 141.5, 141.6, 141.8, 141.9, 142.1, 142.3, 142.4 (2C), 143.0, 144.3, 144.5, 145.2 (2C), 145.3, 145.5, 146.0 (2C), 146.1, 146.2, 146.4, 146.9, 147.0, 147.2, 153.9, 154.2, 170.5; HRMS (FAB) *m/z* 996.1210 (M+1, C₇₃H₁₇F₃NO₂ requires 996.1211).

37: ¹H-NMR 0.5 (s, 9H), 1.18 (t, 3H, *J* = 7.2 Hz), 4.20 (q, 1H, *J* = 7.2 Hz), 4.28 (q, 1H, *J* = 7.2 Hz), 4.65 (d, 1H, *J* = 13.8 Hz), 5.33 (d, 1H, *J* = 13.8 Hz), 5.37 (s, 1H), 5.39 (s, 1H), 7.70 (d, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (CDCl₃+CS₂) 0.7, 14.2, 55.8, 61.0, 70.0, 76.7, 77.0, 77.7 125.7 (q, *J* = 14.7 Hz), 128.6, 134.7, 135.6 (d, *J* = 16.5 Hz), 136.2, 139.2, 139.5, 139.6, 140.2, 141.7, 141.8 (2C), 141.9, 142.0, 142.1 (2C), 142.2 (2C), 142.4, 142.6 (2C), 142.7 (2C), 143.0, 143.1, 144.2, 144.3, 144.4, 144.5, 144.8, 145.1 (2C), 145.2 (3C), 145.4, 145.8, 145.9 (2C), 146.1 (2C), 146.2, 146.5, 146.9, 147.0, 152.4, 154.6, 156.2, 156.9, 170.1; HRMS (FAB) *m/z* 1066.1447 (M+1, C₇₆H₂₃ F₃NO₂Si requires 1066.1450).

Photoreaction of C₆₀+23. Formation of 38.^{17a} N₂ saturated condition. 2 h irradiation, 59% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **38** (96 mg, 37%). O₂ saturated condition. 5 h irradiation, 66% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **38** (91 mg, 35%).

Photoreaction of C₆₀+24. Formation of 39. N₂ saturated condition. 2 h irradiation, 60% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **39** (91 mg, 35%). O₂ saturated condition. 5 h irradiation, 67% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **39** (92 mg, 35%).

¹H-NMR 1.34 (t, 3H, *J* = 7.2 Hz), 2.34 (s, 3H), 2.87 (s, 3H), 4.35 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2 Hz), 5.62 (s, 1H), 6.32 (s, 1H), 7.18 (d, 2H, *J* = 8.1 Hz), 7.63 (d, 2H, *J* = 8.1 Hz); ¹³C-NMR (CDCl₃+CS₂) 14.4, 21.3, 35.0, 61.0, 70.8, 76.0, 76.8, 77.3, 129.3, 133.8, 136.0, 138.0, 139.4, 139.9 (2C), 141.4, 141.5, 141.6, 141.7, 141.9 (3C), 142.0 (2C), 142.1 (2C), 142.4, 142.5 (2C), 142.6, 144.2, 144.4, 144.5, 145.0, 145.1 (3C), 145.2, 145.3, 145.4 (2C), 145.5 (2C), 145.8 (2C), 146.0 (2C), 146.2, 146.5, 146.6, 150.8, 153.8, 155.7, 170.9; HRMS (FAB) *m/z* 940.1339 (M+1, C₇₃H₁₈NO₂ requires 940.1338).

Photoreaction of C₆₀+25. Formation of 40. N₂ saturated condition. 2 h irradiation, 60% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **40** (101 mg, 38%). O₂ saturated condition. 5 h irradiation, 70% conversion, column chromatography (CS₂: hexane = 1: 1) to yield **40** (112 mg, 42%).

¹H-NMR 1.34 (t, 3H, *J* = 7.2 Hz), 2.86 (s, 3H), 3.79 (s, 3H), 4.35 (q, 1H, *J* = 7.2 Hz), 4.44 (q, 1H, *J* = 7.2

Hz), 5.63 (s, 1H), 6.32 (s, 1H), 6.91 (d, 2H, $J = 8.7$ Hz), 7.68 (d, 2H, $J = 8.7$ Hz); ^{13}C -NMR ($\text{CDCl}_3 + \text{CS}_2$) 14.4, 34.8, 54.8, 60.8, 70.6, 76.1, 76.7, 77.2, 113.8, 128.7, 130.4, 135.8, 135.9, 136.1, 137.4, 139.4, 139.9 (2C), 141.4, 141.5 (2C), 141.6, 141.8 (2C), 141.9 (2C), 142.0 (3C), 142.4 (2C), 142.5, 142.8, 144.1, 145.0 (2C), 145.1 (2C), 145.3 (3C), 145.4 (2C), 145.7 (2C), 145.9 (2C), 146.0, 146.2, 146.4, 146.5, 153.7, 153.9, 155.7, 159.4, 170.5; HRMS (FAB) m/z 956.1290 (M+1, $\text{C}_{73}\text{H}_{18}\text{NO}_3$ requires 956.1287).

Photoreaction of $\text{C}_{60}+26$. Formation of **41.** N_2 saturated condition. 5 h irradiation, 76% conversion, column chromatography (CS_2 : hexane = 1: 1) to yield **41** (106 mg, 40%). O_2 saturated condition. 5 h irradiation, 60% conversion, column chromatography (CS_2 : hexane = 1: 1) to yield **41** (85 mg, 32%). ^1H -NMR 1.32 (t, 3H, $J = 7.2$ Hz), 2.86 (s, 3H), 4.35 (q, 1H, $J = 7.2$ Hz), 4.44 (q, 1H, $J = 7.2$ Hz), 5.63 (s, 1H), 6.36 (s, 1H), 7.07 (t, 2H, $J = 8.7$ Hz), 7.76 (t, 2H, $J = 8.7$ Hz); ^{13}C -NMR ($\text{CDCl}_3 + \text{CS}_2$) 14.3, 34.8, 60.9, 70.5, 75.7, 76.6 (2C), 115.4 (d, $J = 87.6$ Hz), 130.8 (d, $J = 30.2$ Hz), 132.5 (2C), 135.8, 136.0 (d, $J = 20.7$ Hz), 137.3, 139.3, 139.4, 139.9 (2C), 141.3, 141.4, 141.5, 141.7, 141.8, 141.9 (4C), 142.3, 142.4, 142.5, 142.9, 144.1, 144.2, 144.3, 144.4, 144.9, 145.0 (2C), 145.1, 145.2, 145.3 (3C), 145.4, 145.5, 145.7 (2C), 145.9 (3C), 146.0, 146.1, 146.2, 147.0, 147.2, 150.4, 153.2, 153.3, 155.4, 162.4 (d, $J = 985.8$ Hz), 170.5; HRMS (FAB) m/z 944.1089 (M+1, $\text{C}_{72}\text{H}_{15}\text{FNO}_2$ requires 944.1087).

Photoreaction of $\text{C}_{60}+27$. Formation of **42.** N_2 saturated condition. 5 h irradiation, 72% conversion, column chromatography (CS_2 : hexane = 1: 1) to yield **42** (117 mg, 42%). O_2 saturated condition. 5 h irradiation, 57% conversion, column chromatography (CS_2 :hexane = 1: 1) to yield **42** (89 mg, 32%); 8 h irradiation, 85% conversion, column chromatography (CS_2 :hexane = 1: 1) to yield **42** (139 mg, 50%). ^1H -NMR 1.34 (t, 3H, $J = 7.2$ Hz), 2.87 (s, 3H), 4.36 (q, 1H, $J = 7.2$ Hz), 4.44 (q, 1H, $J = 7.2$ Hz), 5.54 (s, 1H), 6.45 (s, 1H), 7.65 (d, 2H, $J = 8.4$ Hz), 7.92 (d, 2H, $J = 8.4$ Hz); ^{13}C -NMR ($\text{CDCl}_3 + \text{CS}_2$) 14.4, 29.7, 34.9, 61.1, 70.8, 75.6, 76.8, 77.2, 125.4 (q, $J = 14.7$ Hz), 129.7, 136.0 (2C), 136.2, 137.3, 139.4, 139.5, 140.0, 141.2, 141.5 (2C), 141.6 (2C), 141.7, 141.8, 141.9, 142.0 (2C), 142.5 (2C), 142.6, 142.9 (2C), 143.0, 144.2, 144.3, 144.4 144.9, 145.0, 145.1 (2C), 145.2, 145.3, 45.4, 145.5, 145.8 (2C), 146.0 (2C), 146.1 (2C), 146.2 (2C), 147.2, 147.3, 150.4, 152.8, 153.0, 155.3, 170.7; HRMS (FAB) m/z 994.1052 (M+1, $\text{C}_{73}\text{H}_{15}\text{F}_3\text{NO}_2$ requires 994.1055).

Photoreactions of C_{60} with Amine **6 in a completely deoxygenate solution.** A 10% EtOH-toluene solution (7 mL) containing C_{60} (1.73×10^{-4} M) and amine **6** (3.46×10^{-4} M) was added to a Schlenk flask. The flask containing the solution immersed in liquid nitrogen evacuated using a vacuum and pump for 20 min. The solution was thawed and then subjected to 3 repeated freeze-pump-thaw cycles until evolution of gas during thawing was not observed. The flask was filled with N_2 gas and then sealed. Irradiation (>300 nm) for 2.5 h gave a photolysate that was subjected to HPLC analysis. The results show that a single peak corresponding to aminomethyl-fullerene **28** is present in the chromatogram.

ACKNOWLEDGEMENTS

We congratulate Professor Lutz F. Tietze on the occasion of his 75th birthday. This study was supported by a 2014 Yeungnam University Research Grant (214A380001).

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