SYNTHESIS OF FUNCTIONALIZED FULLERENES BY PHOTOADDITION OF \(N\-\alpha\-\)TRIMETHYLSILYL-\(N\-CARBOXYMETHYL-N\-BENZYLAMINES\) TO \(C_{60}\)

Suk Hyun Lim,1 Dae Won Cho,1* and Patrick S. Mariano2*

1Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea. 2Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, USA; E-mail: mariano@unm.edu

Abstract – Photoaddition reactions of fullerene \(C_{60}\) with \(N\-\alpha\-\)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 \(\alpha\-trimethylsilyl-aminium\) radicals and the \(C_{60}\) anion radical by SET from the amines to the triplet excited state of \(C_{60}\). This step is followed by desilylation to produce \(\alpha\-amino\) radicals. Coupling of these radicals with the anion radical of \(C_{60}\) followed by protonation or with the hydrofullerene radical generated by protonation of the anion radical of \(C_{60}\) then produces aminomethyl-1,2-dihydrofullerenes. When limited amounts of \(^3\)O\(_2\) 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 \(N\-\alpha\-\)trimethylsilyl-\(N\-carboxymethyl-N\-benzylamines\) to produce azomethine ylide intermediates. Dipolar cyloaddition of the ylides to \(C_{60}\) then produces fulleropyrrolidines. Photoreactions of the \(C_{60}\) and the amines in the presence of high \(^3\)O\(_2\) concentrations exclusively produce fulleropyrrolidine. In addition, the results show that photoreactions of non-silicon substituted, \(N\-methyl-N\-carboxymethyl-N\-benzylamines\) with \(C_{60}\) form fulleropyrrolidines.
independent of the concentration of \( \text{O}_2 \) 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 substances\(^14\),\(^15\) also serve as useful methods for synthesizing substituted fullerenes. These reactions are driven by the high electron affinities\(^18\) and relatively high reduction potential \((^3\text{E}_{\text{red}}(C_{60}) = 1.14 \text{ V vs SCE})\)\(^19\) of the triplet excited state of \(C_{60}\). Observations made in earlier studies\(^17\) show that SET promoted photoaddition reactions take place between tertiary amines and fullerene to produce aminomethyl substituted 1,2-dihydrofullerene derivatives. Moreover, when \(\alpha\)-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 \(\alpha\)-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](image_url)

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 \(N\)-\(\alpha\)-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 \( N\)\( -\alpha \)-trimethylsilyl-\( N\)\( ,N\)-dibenzylamines, which contain electron withdrawing phenyl substituents \( \text{(i.e., F, CF}_3\text{)} \), require longer irradiation times and produce 1,2-adducts in low yields.\(^{17b}\) In addition, photoreactions of deoxygenated solutions of \( C_{60} \) and benzylamines, which contain electron withdrawing \( N\)-carboxymethyl groups \( \text{(e.g. 6 in Scheme 2)} \), not only require longer irradiation times and they produce either low yields of aminomethyl-1,2-dihydrofullerene adducts (under \( N_2 \) purged 10% EtOH-toluene) or fulleropyrrolidines \( \text{(e.g. 7 in Scheme 2)} \) 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 \( (1^1 O_2) \) mediated generation of azomethine ylides \( \text{(e.g. 8 in Scheme 2)} \), reactive intermediates that undergo 1,3-dipolar cycloadditions to fullerene.\(^{7\text{-}9,17}\)

![Scheme 2](image_url)

The unique effects of \( N\)-carboxymethyl substituents on the nature of photochemical reactions of amines with \( C_{60} \) and substituent effects on efficiencies of SET promoted photochemical reactions of \( C_{60} \) with tertiary \( N\)-\( \alpha \)-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 \( C_{60} \) with electron donating and withdrawing \( \text{para-phenyl} \) substituted \( N\)-carboxymethyl-\( N\)-\( \alpha \)-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 \( \alpha \)-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 \( C_{60} \) 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 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 $\text{K}_2\text{CO}_3$ 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).

<table>
<thead>
<tr>
<th>Substrates</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>Benzylamines</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>H</td>
<td>SiMe$_3$</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>Me</td>
<td>SiMe$_3$</td>
<td>19</td>
</tr>
<tr>
<td>11</td>
<td>OMe</td>
<td>SiMe$_3$</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>F</td>
<td>SiMe$_3$</td>
<td>21</td>
</tr>
<tr>
<td>13</td>
<td>CF$_3$</td>
<td>SiMe$_3$</td>
<td>22</td>
</tr>
<tr>
<td>14</td>
<td>H</td>
<td>H</td>
<td>23</td>
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<tr>
<td>15</td>
<td>Me</td>
<td>H</td>
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<td>OMe</td>
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<td>17</td>
<td>F</td>
<td>H</td>
<td>26</td>
</tr>
<tr>
<td>18</td>
<td>CF$_3$</td>
<td>H</td>
<td>27</td>
</tr>
</tbody>
</table>

Scheme 3

Photoreactions of $\text{C}_6\text{O}_6$ with $N$-α-trimethylsilyl-$N$-carboxymethyl-$N$-benzylamines and non-trimethylsilyl containing counterparts. The yields and product distributions of photoreactions of $\text{C}_6\text{O}_6$ 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 $\text{C}_6\text{O}_6$ (0.28 mmol) and benzylamines (0.59 mmol). The photolysates were triturated with CHCl$_3$ to recover $\text{C}_6\text{O}_6$ 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 $^1\text{H}$ and $^{13}\text{C}$ 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\textsubscript{60} with α-trimethylsilyl containing benzylamines 6, and 19-22, carried out on N\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{60} with electron withdrawing group (F and CF\textsubscript{3}) substituted benzylamines 21 and 22 (entries 4-5, Table 1) require longer irradiation times to bring about high C\textsubscript{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,\textsuperscript{17a} showing that aminomethyl-1,2-dihydrofullerene 28\textsuperscript{17a} is not converted to fulleropyrrolidine 33\textsuperscript{17a} upon prolonged photoirradiation, demonstrate that two types of adducts formed in these photoreactions arise by independent pathways.

![Scheme 4](image)

**Table 1.** Products and yields of photoaddition reactions of N\textsubscript{2} purged 10% EtOH-toluene solutions containing C\textsubscript{60} and 6 and 19-22.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Irradiation Time (h)</th>
<th>Conversion (%)</th>
<th>Product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>1</td>
<td>95</td>
<td>28 (68), 33 (10)</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
<td>1</td>
<td>100</td>
<td>29 (69), 34 (2)</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1</td>
<td>100</td>
<td>30 (70), 35 (3)</td>
</tr>
<tr>
<td>4</td>
<td>21</td>
<td>3</td>
<td>89</td>
<td>31 (57), 36 (10)</td>
</tr>
<tr>
<td>5</td>
<td>22</td>
<td>3</td>
<td>77</td>
<td>32 (40), 37 (10)</td>
</tr>
</tbody>
</table>
We postulated that the small yet finite amounts of \( \text{O}_2 \), 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 \( \text{C}_{60} \) with \( \alpha \)-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 \( \text{C}_{60} \) (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 \( \text{O}_2 \) completely. Irradiation of this solution under a \( \text{N}_2 \) 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 \( \text{C}_{60} \) 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 \( \text{O}_2 \) purged 10% EtOH-toluene solutions containing \( \text{C}_{60} \) and 6 and 19-22.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Irradiation Time (h)</th>
<th>Conversion (%)(^b)</th>
<th>Product (%)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>2</td>
<td>89</td>
<td>33 (57)</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
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<td>34 (56)</td>
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<td>56</td>
<td>37 (32)</td>
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<td>7</td>
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<td>4</td>
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<td>37 (51)</td>
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<tr>
<td>8(^d)</td>
<td>6</td>
<td>2</td>
<td>91</td>
<td>38 (70)</td>
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</tbody>
</table>

\(^a\)\(\alpha\)-Silylamines (0.56 mmol) and \( \text{C}_{60} \) (0.28 mmol) in 220 mL of 10% EtOH-toluene. 
\(^b\)Conversions determined based on recovered \( \text{C}_{60} \). 
\(^c\)Yields of isolated products. 
\(^d\)Previous 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 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Irradiation Time (h)</th>
<th>Conversion (%)$^b$</th>
<th>Product (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>2</td>
<td>59</td>
<td>38 (37)</td>
</tr>
<tr>
<td>2</td>
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<td>2</td>
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<td>40 (38)</td>
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<td>41 (40)</td>
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<td>5</td>
<td>27</td>
<td>5</td>
<td>72</td>
<td>42 (42)</td>
</tr>
<tr>
<td>6$^d$</td>
<td>23</td>
<td>2</td>
<td>55</td>
<td>38 (30)</td>
</tr>
</tbody>
</table>

$^a$Amines (0.56 mmol) and C$_{60}$ (0.28 mmol) in 220 mL of 10% EtOH-toluene.
$^b$Conversions determined based on recovered C$_{60}$. $^c$Yields of isolated products. $^d$Previous 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Irradiation Time (h)</th>
<th>Conversion (%)$^b$</th>
<th>Product (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>5</td>
<td>66</td>
<td>38 (35)</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>5</td>
<td>67</td>
<td>39 (35)</td>
</tr>
</tbody>
</table>
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 \( N \)-\( \alpha \)-trimethylsilyl-\( N \)-carboxymethyl-\( N \)-benzylamines plays a surprisingly important role in governing efficiencies of photoaddition reactions with \( C_{60} \). 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 \( C_{60} \) 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 \( C_{60} \), produced by direct excitation followed by rapid intersystem crossing. Because the rates of SET from all benzylamines to the triplet excited state of \( C_{60} \) 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 \( C_{60} \). Alternatively, the substituents could influence the rates of \( \alpha \)-amino radical coupling with the anion radical of \( C_{60} \) 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 \( N \)-\( \alpha \)-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 familiar\(^{7,9}\) dipolar cycloadditions to \( C_{60} \) (Scheme 2). As suggested by Foote\(^{20a}\) earlier, the triplet excited state of \( C_{60} \) should undergo energy transfer to \( ^3\)O\(_2\) to form \( ^1\)O\(_2\) and ground-state \( C_{60} \), a process that competes with or dominates over SET from the amine depending upon the concentration of \( ^3\)O\(_2\). In the manner described by Foote,\(^{20a}\) \( ^1\)O\(_2\) then reacts with the \( N \)-carboxymethyl-\( N \)-\( \alpha \)-trimethylsilyl-\( N \)-benzylamine through

\[
\begin{array}{cccccc}
3 & 25 & 5 & 70 & 40 (42) \\
4 & 26 & 5 & 60 & 41 (32) \\
5 & 27 & 5 & 57 & 42 (32) \\
6 & 27 & 8 & 85 & 42 (50) \\
\end{array}
\]

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

\(^b\)Conversions determined based on recovered \( C_{60} \).

\(^c\)Yields of isolated products.
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^O_2 is produced from small amounts of ^3^O_2 present under these conditions. Owing to the fact that aminomethyl-1,2-dihydrofullerene production is highly inefficient in these cases, fullerpyrrolidine 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^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 alkoxycarbonyl substituted α-carbons and not the benzylic position of the amines (see Scheme 2). However, in ^1^O_2 promoted reactions of the non-trimethylsilyl substituted amines H-atom abstractions occurs at the amine alkoxycarbonyl and aryl substituted α-centers exclusively to generate α-amino radicals 43 and 44 and, eventually, azomethine ylide 45 (Scheme 6).

![Scheme 6](image)

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 O2.

EXPERIMENTAL

General Procedure 1H and 13C NMR spectra were recorded on CDCl3 solutions and chemical shifts are reported in parts per million relative to CHCl3 (7.24 ppm for 1H and 77.0 ppm for 13C) 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 K2CO3 (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 CH2Cl2. 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); 13C-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, C16H27NO2Si 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), 4.12 (q, 2H, J = 7.2 Hz), 6.82 (d, 2H, J = 8.7 Hz), 7.24 (d, 2H, J = 8.7 Hz); 13C-NMR -1.5, 14.3, 45.5, 55.1, 56.8, 59.9, 60.7, 113.5, 129.5, 131.4, 158.6, 171.4; HRMS (EI) m/z 309.1757 (M, C16H27NO3Si 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); 13C-NMR -1.7, 14.1, 45.3, 56.8, 59.8, 60.6, 114.8 (d, J = 38.7 Hz), 130.1 (d, J = 31.5 Hz), 135.1 (d, J = 12 Hz), 161.8 (d, J = 792.3 Hz), 171.7; HRMS (EI) m/z 297.1562 (M, C15H24FNO2Si 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); 13C-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, C16H24F3NO2Si requires 347.1528).
Photoreactions of C$_{60}$ 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 C$_{60}$ (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 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 generate the pure photoproducts.

Photoreaction of C$_{60}$ with Amine 6. Formation of 28 and 33. N$_2$ saturated condition. 1 h irradiation, 95% conversion, column chromatography (CS$_2$: hexane = 1: 1) to yield 28 (175 mg, 68%) and 33 (27 mg, 10%). O$_2$ saturated condition. 2 h irradiation, 88% conversion, column chromatography (CS$_2$: hexane = 1: 1) to yield 33 (157 mg, 57%).

Photoreaction of C$_{60}$+19. Formation of 29 and 34. N$_2$ saturated condition. 1 h irradiation, 100% conversion, column chromatography (CS$_2$: hexane = 1: 1) to yield 29 (179 mg, 69%) and 34 (7 mg, 2%). O$_2$ saturated condition. 2 h irradiation, 90% conversion, column chromatography (CS$_2$: hexane = 1: 1) to yield 34 (158 mg, 56%).

29: $^1$H-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); $^{13}$C-NMR (CDCl$_3$+CS$_2$) 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, C$_{73}$H$_{20}$NO$_2$ requires 942.1494).

34: $^1$H-NMR 0.51 (s, 9H), 1.17 (t, 3H, $J = 7.2$ Hz), 2.40 (s, 3H), 4.17 (q, 2H, $J = 7.2$ 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); $^{13}$C-NMR (CDCl$_3$+CS$_2$) 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, 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, C$_{76}$H$_{26}$NO$_2$Si requires 1012.1733).

Photoreaction of C$_{60}$+20. Formation of 30 and 35. N$_2$ saturated condition. 1 h irradiation, 100% conversion, column chromatography (CS$_2$: hexane = 1: 1) to yield 30 (186 mg, 70%) and 35 (8 mg, 3%). O$_2$ saturated condition. 2 h irradiation, 90% conversion, column chromatography (CS$_2$: hexane = 1: 1) to yield 35 (163 mg, 57%).
30: $^{1}$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); $^{13}$C-NMR (CDCl$_3$+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, C$_{73}$H$_{20}$NO$_3$ requires 958.1443).

35: $^{1}$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); $^{13}$C-NMR (CDCl$_3$+CS$_2$) 0.7, 14.1, 55.0, 55.4, 60.7, 69.8, 76.1, 77.5, 77.8, 114.1, 129.7, 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, 145.4 (2C), 145.5 (3C), 145.4, 145.7, 145.8 (2C), 145.9, 146.0 (2C), 146.1, 146.3, 146.5, 146.8, 146.9152.7, 154.9, 156.4, 157.2, 159.1, 170.3; HRMS (FAB) $m/z$ 10.28.1685 (M$^+$+1, C$_{76}$H$_{26}$NO$_3$Si requires 1028.1682).

Photoreaction of C$_{60}$+21. Formation of 31 and 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: $^{1}$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); $^{13}$C-NMR (CDCl$_3$+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, C$_{72}$H$_{17}$NO$_2$F requires 946.1243).

36: $^{1}$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); $^{13}$C-NMR (CDCl$_3$+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, C$_{75}$H$_{23}$FNO$_2$Si requires 1016.1482).
Photoreaction of $C_{60}^+$. Formation of $32$ and $37$. $N_2$ saturated condition. 3 h irradiation, 77% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $32$ (112 mg, 40%) and $37$ (30 mg, 10%). $O_2$ saturated condition. 2 h irradiation, 56% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $37$ (96 mg, 32%); 4 h irradiation, 81% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $37$ (141 mg, 51%).

$32$: $^1$H-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); $^{13}$C-NMR ($CDCl_3+CS_2$) 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, 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) $m/z$ 996.1211 ($M+1$, $C_{73}H_{17}F_3NO_2$ requires 996.1211).

$37$: $^1$H-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), 7.70 (d, 2H, $J = 8.4$ Hz), 7.78 (d, 2H, $J = 8.4$ Hz); $^{13}$C-NMR ($CDCl_3+CS_2$) 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 ($M+1$, $C_{76}H_{23}F_3NO_2Si$ requires 1066.1450).

Photoreaction of $C_{60}^+$. Formation of $38$. $N_2$ saturated condition. 2 h irradiation, 59% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $38$ (96 mg, 37%). $O_2$ saturated condition. 5 h irradiation, 66% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $38$ (91 mg, 35%).

$38$: $^1$H-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); $^{13}$C-NMR ($CDCl_3+CS_2$) 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 ($M+1$, $C_{73}H_{18}NO_2$ requires 940.1338).

Photoreaction of $C_{60}^+$. Formation of $40$. $N_2$ saturated condition. 2 h irradiation, 60% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $40$ (101 mg, 38%). $O_2$ saturated condition. 5 h irradiation, 70% conversion, column chromatography ($CS_2$: hexane = 1: 1) to yield $40$ (112 mg, 42%).

$1^H$-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).
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 (CDCl\(_3\)+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, \( C_{73}H_{18}NO_3 \) requires 956.1287).

**Photoreaction of C\(_{60}\)+26. Formation of 41.** \( \text{N}_2 \) saturated condition. 5 h irradiation, 76% conversion, column chromatography (CS\(_2\): hexane = 1: 1) to yield 41 (106 mg, 40%). \( \text{O}_2 \) saturated condition. 5 h irradiation, 60% conversion, column chromatography (CS\(_2\): hexane = 1: 1) to yield 41 (85 mg, 32%).

**Photoreaction of C\(_{60}\)+27. Formation of 42.** \( \text{N}_2 \) saturated condition. 5 h irradiation, 72% conversion, column chromatography (CS\(_2\): hexane = 1: 1) to yield 42 (117 mg, 42%). \( \text{O}_2 \) 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%).

**Photoreactions of C\(_{60}\) with Amine 6 in a completely deoxygenate solution.** A 10% EtOH-toluene solution (7 mL) containing C\(_{60}\) (1.73 x 10\(^{-4}\) M) and amine 6 (3.46 x 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 \( \text{N}_2 \) 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).

REFERENCES


