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Photoaddition reactions of azomethine ylides generated from α-aminonitriles to fullerene C_{60}: Formation of fulleropyrrolidines and reaction efficiencies changes depending on reaction conditions

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ABSTRACT

Photoaddition reactions of C_{60} with both (trimethylsilyl)methyl and either benzyl or phenethyl group containing α-aminonitriles were carried out to explore how product distributions and reaction efficiencies can be influenced by reaction solvent systems. The results show that photoreactions produce both trimethylsilyl- and cyano group containing fulleropyrrolidines as a major (or exclusive) product. Especially, photoreactions performed in either EtOH containing solution or oxygenated environment take place with a much more efficient manner.

Chemical modification of carbon sp^2-orbitals conjugated, spherical fullerene surface at 6,6-junction position through thermochemical- and photochemical introduction of mono- and multi organic moieties have drawn great attention since the discovery of unique fullerene chemical/physical characteristics [1–4]. Especially, functionalized organofullerenes possessing amino moiety are important and popular due to their synthetic accessibility and well-defined structures. Among the amino group containing organofullerenes, the five-membered *N*-heterocyclic pyrrolidine ring fused fullerenes, fulleropyrrolidines, are one of the most extensively studied compounds after the pioneering work of Prato and his colleagues, in which thermochemically generated azomethine ylides from amino acid derivatives were cycloadded to fullerene C_{60} [5]. Since then, a variety of synthetic methods involving a formation of azomethine ylide intermediates have been developing to prepare fulleropyrrolidines with a structural diversity so far [6–10]. In our recent study [11], we showed that α-aminonitrile substrates could serve as an efficient precusor for azomethine ylides and, in addition, these in situ generated azomethine ylide intermediates could be added to fullerene C_{60} to form fulleropyrroldines with an efficient and stereoselective manner. Thus, as a continuing research program aiming at developing novel types of functionalized fullerene derivatives, we've prepared both (trimethylsilyl)methyl ($TMSCH_2$-) and either benzyl ($PhCH_2$-) or phenethyl ($PhCH_2CH_2$-) group containing α-aminonitriles and carried out photochemical reactions with these substrates in the presence of C_{60} to see how photoproduct distributions and reaction efficiencies can be varied depending on reaction conditions employed.

For the photochemical reactions, firstly, a series of α-aminonitriles possessing both (trimethylsilyl)methyl- and benzyl/phenethyl-moiety, were prepared by using well-known base catalyzed nucleophilic substitution reactions [11,12]. Specifically, K_2CO_3-catalyzed reactions of benzyl/phenethyl amines with (iodomethyl)trimethylsilane ($TMSCH_2I$) gave rise to formation of high yielding of *N*-(trimethylsilyl)methyl substituted amines. Then, after purification, the resulting secondary amines were further reacted with $BrCH_2CN$ in the presence of base (K_2CO_3) to yield target α-aminonitriles **13a-13f**. (Scheme 1)

Next, photochemical reactions of C_{60} (0.28 mmol) and synthesized α-aminonitriles (0.56 mmol) were carried out by using 450 W Hanovia medium pressure mercury lamp equipped with flint glass filter (>310 nm) under either deoxygenated (N_2-purged) or oxygenated (O_2-pured) solution. In addition, as a reaction solvent, pure toluene, 10% EtOH-toluene (v/v) and 10% EtOH-*o*-dichlorobenzene (ODCB) (v/v) solution were employed to explore how the photoproduct distributions and reaction efficiencies are affected by solvent system. After photoirradiation of solutions for a certain period time, the photolysates were then isolated by using column chromatography to determine photoproducts and their chemical yields.

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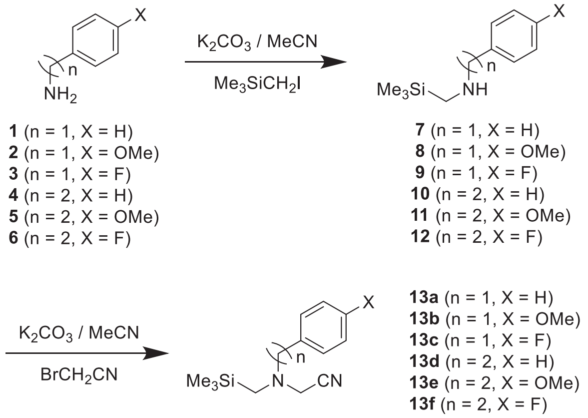
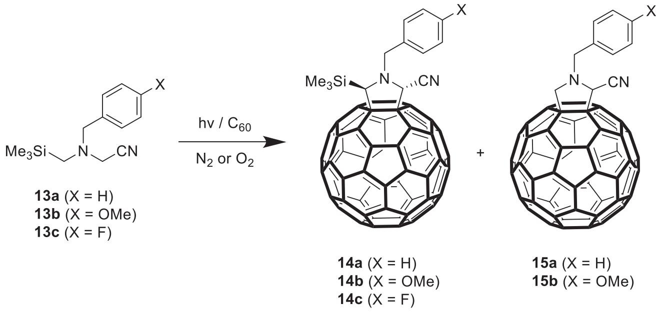


Scheme 1. Preparation of α-aminonitrile substrates **13a-13f**.

Firstly, photoreactions of C_{60} with α-aminonitriles **13a-13c** [11a], bearing both $TMSCH_2$ and benzyl group, were performed. In the N_2-purged condition, as can be seen from Scheme 2 and Table 1, while the photoreactions of pure toluene solution containing non (*p*-H, **13a**)- and *para*-OMe (**13b**) substituted benzylamines and C_{60} produced TMS group containing *trans*-fulleropyrrolidines **14a-14b** [11a] predominantly along with non-TMS containing fulleropyrrolidines **15a-15b** [11a] (entries 1–2), the reaction of *para*-F substituted benzylamine **13c** and C_{60} gave rise to formation of a photoadduct **14c** [11a] solely (entry 3) Noticeably, the reaction of **13c** with C_{60} required much longer irradiation time to bring about high conversion yields [11,13a]. Similar product distribution patterns were observed in the photoreactions of **13a-13c** and C_{60} under the N_2-purged, either 10% EtOH-toluene (entries 4–6) or 10% EtOH-ODCB solution (entries 7–9), albeit yields are a little different. Interesting results made from these photoreactions were that reaction efficiencies (*i.e.*, conversion/product yields vs irradiation time) could be varied depending on reaction solvent system. Especially, reaction efficiencies were improved when polar protic EtOH solvent was added to pure toluene solvent [11a,13b]. It is worthy to mention that neither bis-nor multi-pyrrolidine ring fused photoproducts were observed in current reaction conditions.



Scheme 2. Photochemical reactions of C_{60} with α-aminonitriles **13a-13c**.

In the photoreactions of O_2-purged solutions, both TMS and cyano group containing *trans*-fulleropyrrolidines **14a-14c** were also produced more predominantly or exclusively. (Table 2) Interestingly, the reactions of O_2-purged 10% EtOH-ODCB solutions containing **13a-13c** and C_{60} took place chemoselectively to give **14a-14c** as a sole product. Here, it is worthy to mention that photochemical reaction conducted in O_2-purged condition required less irradiation time to bring about high conversion of starting fullerene C_{60} than those performed in N_2-purged condition did.

Under the nearly equal reaction conditions, photochemical reactions of phenethyl ($PhCH_2CH_2$-) substituted α-aminonitrile analogs **13d-13f** were also performed.

As described in Scheme 3 and Tables 3 and 4, the product distribution profiles arisen from the reactions of **13d-13f** with C_{60} were quite comparable to those observed from the reactions of **13a-13c** with C_{60}. Specifically, when either deoxygenated or oxygenated solutions containing C_{60} and **13d-13f** were irradiated, photoreactions took place to give rise to formation of both TMS and cyano group substituted *trans*-fulleropyrrolidines **14d-14f** with a highly chemo- and stereoselective manner. Equally interesting point was that regardless of the presence of electron withdrawing group (EWG) (*i.e.*, *para*-F) on phenyl ring in **13f**, in which EWG generally cause diminish reaction efficiencies [13a], reaction efficiencies for all of **13d-13f** were quite similar.

The structure of all of photoproducts, **14a-14f** and **15a-15b**, secured in these reactions were clearly assigned by using ^{1}H- and ^{13}C NMR, HRMS and UV–visible spectroscopic methods as well as by comparison of data to those of previously reported fulleropyrrolidine derivatives [7,9,11,14]. In addition, based upon the nuclear overhauser enhancement spectroscopic technique (NOESY) [7a,8c,11a], stereochemistry of photoadducts could be successfully determined as a *trans*-isomer.

As can be seen by viewing the data shown in Table 1–4, we found that both the reaction condition and the structural nature of α-aminonitriles play an important role in governing the irradiation time required to bring about high-yielding conversion- and chemical-yields (*i.e.*, reaction efficiencies). Thus, in order to gain quantitative information about the reaction efficiencies for these photoreactions of **13a-13f** with C_{60}, relative quantum efficiencies (Φ_{rel}) of the photoreactions were determined (see Experimental). Specifically, by setting the Φ_{rel} for the reaction of **13c** with C_{60} under the N_2-purged 10% EtOH-ODCB solution to be unity ($\Phi_{rel} = 1$), Φ_{rel} for all of amines **13a-13f** was then determined.

Table 1
Product and yields of photoreactions of C_{60} with α-aminonitriles **13a-13c** in deoxygenated (N_2-purged) condition.[a]

Entry	Amine	Reaction condition	Irradiation time (h)	Conversion (%)[b]	Yield (%)[c]
1	**13a**	Toluene	2	77	**14a** (32), **15a** (2)
2	**13b**	Toluene	2	78	**14b** (24), **15b** (3)
3	**13c**	Toluene	6	50	**14c** (15)
4	**13a**	10% EtOH-toluene	2	83	**14a** (42), **15a** (11)
5	**13b**	10% EtOH-toluene	2	85	**14b** (44), **15b** (15)
6	**13c**	10% EtOH-toluene	6	69	**14c** (41)
7	**13a**	10% EtOH-ODCB	3	87	**14a** (40), **15a** (3)
8	**13b**	10% EtOH-ODCB	3	89	**14b** (47), **15b** (1)
9	**13c**	10% EtOH-ODCB	6	62	**14c** (30)

[a] 220 mL of solutions containing C_{60} (0.28 mmol) and α-aminonitriles (0.56 mmol) were irradiated during the given period time.
[b] Conversion yield was determined by recovered C_{60}.
[c] Isolation yields.

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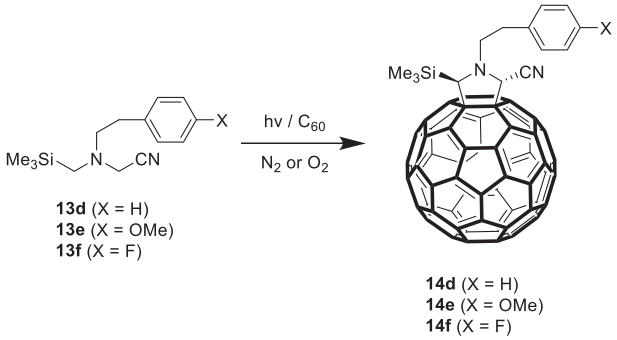
Table 2
Product and yields of photoreactions of C_{60} with α-aminonitriles **13a**-**13c** in oxygenated (O_2-purged) condition.[a]

Entry	Amine	Reaction condition	Irradiation time (h)	Conversion (%)[b]	Yield (%)[c]
1	**13a**	toluene	1	93	**14a** (46), **15a** (2)
2	**13b**	toluene	1	95	**14b** (43), **15b** (6)
3	**13c**	toluene	3	85	**14c** (38)
4	**13a**	10% EtOH-toluene	1	94	**14a** (42), **15a** (4)
5	**13b**	10% EtOH-toluene	1	96	**14b** (48), **15b** (4)
6	**13c**	10% EtOH-toluene	3	86	**14c** (41)
7	**13a**	10% EtOH-ODCB	2	85	**14a** (44)
8	**13b**	10% EtOH-ODCB	2	97	**14b** (50)
9	**13c**	10% EtOH-ODCB	5	88	**14c** (48)

[a] 220 mL of solutions containing C_{60} (0.28 mmol) and α-aminonitriles (0.56 mmol) were irradiated during the given period time.
[b] Conversion yield was determined by recovered C_{60}.
[c] Isolation yields.



13d (X = H)
13e (X = OMe)
13f (X = F)

14d (X = H)
14e (X = OMe)
14f (X = F)

Scheme 3. Photochemical reactions of C_{60} with α-aminonitriles **13d**-**13f**.

(Table 5). As depicted in Table 5, the results clearly showed that 1) under the same environment (either O_2 or N_2-purged), the efficiencies of photoreactions performed under the 10% EtOH-toluene solution were much higher than those under the 10% EtOH-ODCB and 2) benzyl substituted α-aminonitriles are more reactive than phenethyl substituted analogs in case that phenyl rings contain either non (H)- or *p*-OMe group. However, it was the other way around when phenyl rings have electron withdrawing p-F substituent.

In here, it is noteworthy to compare photochemical reactions of α-aminonitriles with those of α-aminoesters because α-aminoesters possessing vulnerable α-CH hydrogens ($pK_a \sim$ *ca.* 25) can also serve as a precusor of fulleropyrroldines. Under the equal reaction conditions employed in above reactions, photoreactions of C_{60} with α-aminoesters having the same substituents at nitrogen atom (*i.e.*, both $TMSCH_2$ and either $PhCH_2$ or $PhCH_2CH_2$ group) were performed and then, the product yields and product distribution patterns were analyzed. (Scheme 4 and Table 6) In contrast to the results from the reactions of structurally similar α-aminonitriles **13a** and **13d**, photoreactions of N_2-purged either 10% EtOH-toluene or 10% EtOH-ODCB solutions of C_{60} and **16a**-**16b** produced aminomethylated 1,2-dihydrofullerenes **17a**-**17b** predominantly,

Table 3
Product and yields of photoreactions of C_{60} with α-aminonitriles **13d**-**13f** in deoxygenated (N_2-purged) condition.[a]

Entry	Amine	Reaction condition	Irradiation time (h)	Conversion (%)[b]	Yield (%)[c]
1	**13d**	Toluene	2	60	**14d** (30)
2	**13e**	Toluene	2	60	**14e** (29)
3	**13f**	Toluene	2	57	**14f** (29)
4	**13d**	10% EtOH-toluene	2	70	**14d** (35)
5	**13e**	10% EtOH-toluene	2	68	**14e** (29)
6	**13f**	10% EtOH-toluene	2	64	**14f** (33)
7	**13d**	10% EtOH-ODCB	3	79	**14d** (45)
8	**13e**	10% EtOH-ODCB	3	80	**14e** (40)
9	**13f**	10% EtOH-ODCB	3	74	**14f** (38)

[a] 220 mL of solutions containing C_{60} (0.28 mmol) and α-aminonitriles (0.56 mmol) were irradiated during the given period time.
[b] Conversion yield was determined by recovered C_{60}.
[c] Isolation yields.

Table 4
Product and yields of photoreactions of C_{60} with α-aminonitriles **13d**-**13f** in oxygenated (O_2-purged) condition.[a]

Entry	Amine	Reaction condition	Irradiation time (h)	Conversion (%)[b]	Yield (%)[c]
1	**13d**	Toluene	1	71	**14d** (44)
2	**13e**	Toluene	1	71	**14e** (40)
3	**13f**	Toluene	1	71	**14f** (40)
4	**13d**	10% EtOH-toluene	1	73	**14d** (44)
5	**13e**	10% EtOH-toluene	1	73	**14e** (41)
6	**13f**	10% EtOH-toluene	1	70	**14f** (41)
7	**13d**	10% EtOH-ODCB	2	80	**14d** (48)
8	**13e**	10% EtOH-ODCB	2	85	**14e** (48)
9	**13f**	10% EtOH-ODCB	2	76	**14f** (43)

[a] 220 mL of solutions containing C_{60} (0.28 mmol) and α-aminonitriles (0.56 mmol) were irradiated during the given period time.
[b] Conversion yield was determined by recovered C_{60}.
[c] Isolation yields.

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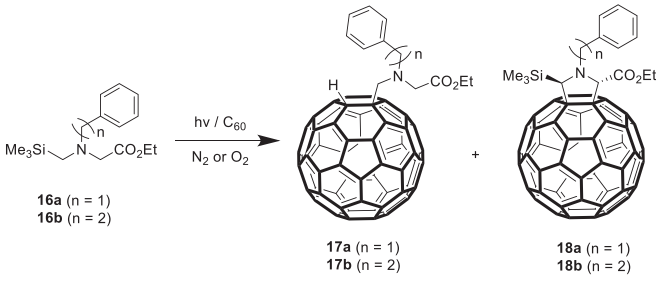
Table 5
Relative quantum efficiencies (Φ_{rel}) of photoreactions of C_{60} with α-aminonitriles **13a-13f**.

Entry	Amine	Reaction condition	Φ_{rel}
1	**13a**	N_2/10% EtOH-toluene	5.1
2	**13b**	N_2/10% EtOH-toluene	4.9
3	**13c**	N_2/10% EtOH-toluene	1.3
4	**13d**	N_2/10% EtOH-toluene	3.4
5	**13e**	N_2/10% EtOH-toluene	3.5
6	**13f**	N_2/10% EtOH-toluene	2.6
7	**13a**	N_2/10% EtOH-ODCB	3
8	**13b**	N_2/10% EtOH-ODCB	3.5
9	**13c**	N_2/10% EtOH-ODCB	1
10	**13d**	N_2/10% EtOH-ODCB	2.9
11	**13e**	N_2/10% EtOH-ODCB	2.9
12	**13f**	N_2/10% EtOH-ODCB	2.5
13	**13a**	O_2/10% EtOH-toluene	7.8
14	**13b**	O_2/10% EtOH-toluene	7.8
15	**13c**	O_2/10% EtOH-toluene	3.1
16	**13d**	O_2/10% EtOH-toluene	5.1
17	**13e**	O_2/10% EtOH-toluene	5.4
18	**13f**	O_2/10% EtOH-toluene	5.1
19	**13a**	O_2/10% EtOH-ODCB	3.9
20	**13b**	O_2/10% EtOH-ODCB	5.2
21	**13c**	O_2/10% EtOH-ODCB	1.5
22	**13d**	O_2/10% EtOH-ODCB	4.2
23	**13e**	O_2/10% EtOH-ODCB	4.2
24	**13f**	O_2/10% EtOH-ODCB	3.9



Scheme 4. Photochemical reactions of C_{60} with α-aminoesters **16a-16b**.

which were not observed in the reaction of **13a** and **13d**, along with fulleropyrrolidines **18a-18b** as a minor adduct. (entries 2–3 and 8–9 in Table 6) Noticeably, EtOH content in solution was inevitable component to bring about conversion of starting fullerene C_{60} and generation of photoproducts in the N_2-purged condition (entries 1 and 7 in Table 6). Photoreactions performed under the O_2-purged conditions were also interesting. For instance, while photoreactions of α-aminoester **16a** required much longer irradiation time, reactions of C_{60} with phenethyl substituted α-aminoester **16b** did not take place even by 5 h irradiation in the presence of molecular oxygen. From the fact that oxidation potentials (E_{ox}) of α-aminonitriles and α-aminoesters have nearly equal values (0.8–1.0 V vs SCE) and single electron transfer (SET) from all of amines to triplet state of C_{60} ($^3C_{60}{}^*$) is thermodynamically favorable, the rates of SET involved in the reactions between amines and triplet state of C_{60} ($^3C_{60}{}^*$) seem to be nearly equal to the diffusion controlled limit [13b]. Thus, the differing in both reaction efficiencies and product distributions observed between α-aminonitriles and α-aminoesters is likely to be the consequence of unequal efficiencies of intermediate forming processes (see below).

Based on photoproduct distributions and the analysis of previously reported studies, we believe that the photochemical reactions of α-aminonitriles **13a-13f** with C_{60} are likely to take place via pathways involving a 1,3-dipolar cycloaddition reaction of in situ generated azomethine ylides to C_{60}. Detail mechanistic pathway is suggested in Scheme 5. Specifically, in the N_2-purged condition, the route involved in the reactions is initiated by a single electron transfer (SET) process occurring from α-aminonitriles **16** to the triplet excited states of C_{60} ($^3C_{60}{}^*$), which are generated by efficient intersystem crossing (ISC) from singlet excited states of C_{60} ($^1C_{60}{}^*$) [15]. Through this SET event, amine radical cations **17** and C_{60} radical anions ($C_{60}{}^{-}$) are formed, in which the generated amine radical cations **17** undergo competitive α-CH deprotonation ($\sim H^+$) or desilylation ($\sim SiMe_3^+$) to produce α-amino radicals **18** and **19** [16]. Noticeably, α-CH deprotonation leading to formation of **19** seems to be more rapid and efficient. Then, sequential SET-deprotonation processes from the generated α-amino radicals can afford the respective 1,3-dipolar azomethine ylides **22** and **23**, which are finally added to C_{60} to yield photoadducts, fulleropyrrolidines **24**. In O_2-purged condition, singlet oxygen ($^1O_2$) is likely to be highly responsible for the generation of azomethine ylides **22** and **23** [17]. Specifically, triplet excited states of C_{60} participate in energy transfer processes in the presence of molecular oxygen ($^3O_2$) to generate singlet oxygen ($^1O_2$). Then, formed singlet oxygen ($^1O_2$) abstract H-atom from α-carbon position to produce α-amino radical intermediates **18** and **19**. Further H-atom abstraction process of **18** and **19** eventually forms azomethine ylides **22** and **23** that serve as a fulleropyrroldine precusor. As an alternative product forming mechanism, stepwise addition of α-amino radicals to fullerene following successive cyclization may be also possible [18]. A further

Table 6
Product and yields of photoreactions of C_{60} with α-aminoesters **16a-16b**.[a]

Entry	Amine	Reaction condition	Irradiation time (h)	conversion (%)[b]	Yield (%)[c]
1	**16a**	N_2, toluene	5	–[d]	–[d]
2[e]	**16a**	N_2, 10% EtOH-toluene	1	95	**17a** (68), **18a** (10)
3	**16a**	N_2, 10% EtOH-ODCB	2	88	**17a** (60), **18a** (10)
4[f]	**16a**	O_2, toluene	5	85	**18a** (50)
5[e]	**16a**	O_2, 10% EtOH-toluene	2	89	**18a** (57)
6	**16a**	O_2, 10% EtOH-ODCB	4	80	**18a** (55)
7	**16b**	N_2, toluene	5	–[d]	–[d]
8	**16b**	N_2, 10% EtOH-toluene	1	93	**17b** (42), **18b** (11)
9	**16b**	N_2, 10% EtOH-ODCB	2	87	**17b** (40), **18b** (8)
10	**16b**	O_2, toluene	5	–[d]	–[d]
11	**16b**	O_2, 10% EtOH-toluene	5	–[d]	–[d]
12	**16b**	O_2, 10% EtOH-ODCB	5	–[d]	–[d]

[a] 220 mL of solutions containing C_{60} (0.28 mmol) and α-aminonitriles (0.56 mmol) were irradiated during the given period time.
[b] Conversion yield was determined by recovered C_{60}.
[c] Isolation yields.
[d] No reaction.
[e] Data from Ref. [9c].
[f] Data from Ref. [11a].

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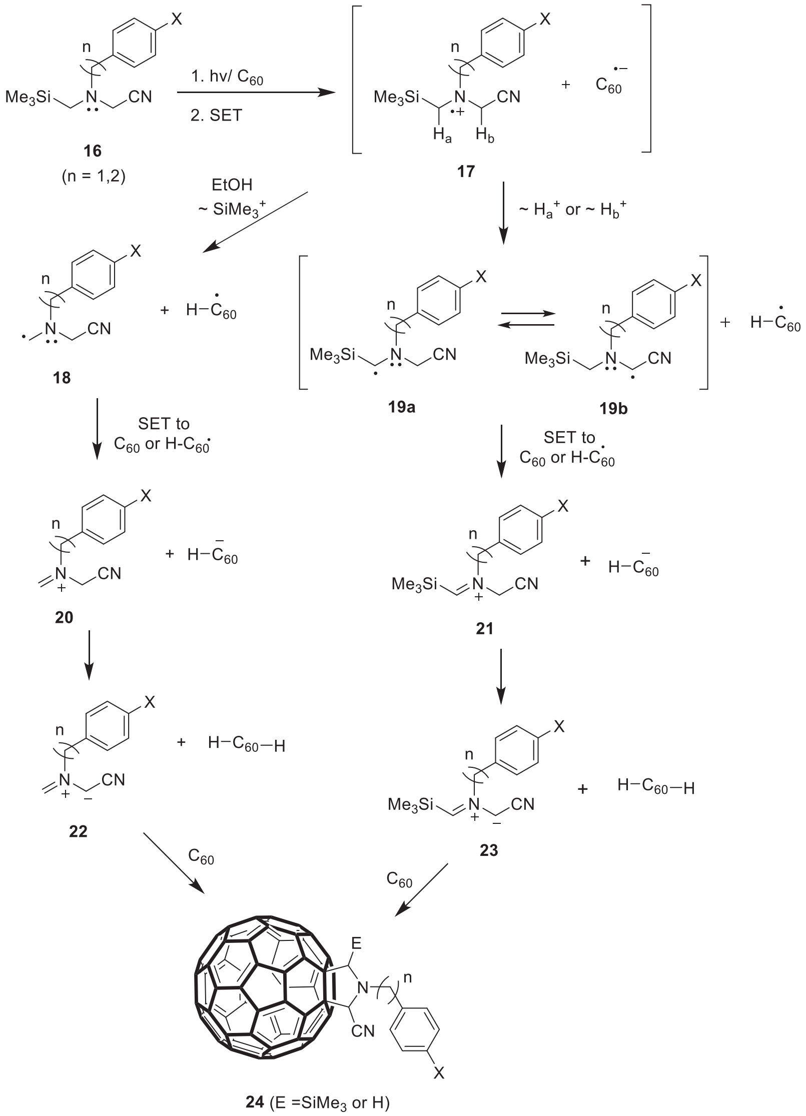

Scheme 5. Mechanistic pathways of photochemical reactions of C_{60} with α-aminonitriles **16** leading to fulleropyrrolidine formation.

studies are underway to elucidate mechanistic pathways involved in fulleropyrrolidin forming processes.

In summary, photochemical reactions of C_{60} with both (trimethylsilyl)methyl and either benzyl or phenethyl group containing α-aminonitriles were conducted to explore how product distributions and reaction efficiencies can be influenced by reaction solvent systems. The results show that product distributions and reaction efficiencies are dependent on reaction conditions and the nature of α-aminonitriles. Especially, the presence of EtOH content in solvent and oxygen environment can facilitate fulleropyrrolidine formation.

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Appendix A. Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra of **13a-13f**, **16a-16b** and synthesized fulleropyrrolidines **14a-14f** and **15a-15b**, **17a-17b**, and **18a-18b**. NOESY spectrum of **13d** and UV-visible spectra of fulleropyrrolidines **14a-14f** and **15a-15b**.) to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.151208. These data include MOL files and InChiKeys of the most important compounds described in this article.

References

[1] (a) A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T. M. Palstra, A.P. Pamirez, A.R. Kortan, Nature 350 (1990) 600;
(b) T.D. Anthopoulos, C. Tanase, S. Setayesh, E.J. Meijer, J.C. Haummelen, P.W. M. Blom, D.M. de Leeuw, Adv. Mater. 16 (2004) 2174;
(c) Y. Yang, Nature 356 (1992) 585.

[2] (a) P.-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, J.D. Thompson, Science 253 (1991) 301;
(b) G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789.

[3] (a) M. Bendikov, F. Wudl, Chem. Rev. 104 (2004) 4891;
(b) F.G. Brunetti, R. Kumar, F. Wudl, J. Mater. Chem. 20 (2010) 2934;
(c) S. Takenaka, K. Yasmashita, N. Takagi, T. Hatta, O. Tsuge, Chem. Lett. (1999) 321;
(d) S.H. Friedman, D.L. DeCamp, R.P. Sijbesma, G. Srdanov, F. Wudl, G.L. Keyton, J. Am. Chem. Soc. 115 (1993) 6506.

[4] (a) K. Matsumoto, K. Hashimoto, M. Kamo, Y. Uetani, S. Hayase, M. Kawatsura, T. Itoh, J. Mater. Chem. 20 (2010) 9226;
(b) T.B. Singh, N. Marjanovic, G.J. Matt, S. Gunes, N.S. Sariciftci, A.M. Ramil, M. Ramil, A. Andreev, H. Sitter, R. Schwodiauer, S. Bauer, Org. Electron. 6 (2005) 105;
(c) M. Prato, J. Mater. Chem. 7 (1997) 1097.

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[5] (a) M. Prato, M. Maggini, Acc. Chem. Res. 31 (1998) 519;
(b) D.M. Guldi, M. Prato, Acc. Chem. Res. 33 (2000) 695.

[6] (a) M. Maggini, G. Scorrano, M. Prato, J. Am. Chem. Soc. 115 (1993) 9798;
(b) M. Maggini, G. Scorrano, A. Bianco, C. Toniolo, R.P. Sijbesma, F. Wudl, M. Prato, J. Chem. Soc., Chem. Commun. 305 (1994).

[7] (a) J.-L. Shi, X.-F. Zhang, H.-J. Wang, F.-B. Li, X.-X. Zhong, C.-X. Liu, L. Liu, C.-Y. Liu, H.-M. Qin, Y.-S. Huang, J. Org. Chem. 81 (2016) 7662;
(b) P.A. Troshin, A.S. Peregudov, D. Muhlbacher, R.N. Lyubovskaya, Eur. J. Org. Chem. (2005:) 3064.

[8] (a) S.-E. Zhu, X. Cheng, Y.-J. Li, C.-K. Mai, Y.-S. Huang, G.-W. Wang, R.-F. Peng, B. Jin, S.-J. Chu, Org. Biomol. Chem. 10 (2012) 8720;
(b) S. Zhang, L. Gan, C. Huang, M. Lu, J. Pan, X. He, J. Org. Chem. 67 (2002) 883;
(c) J.-L. Shi, F.-B. Li, X.-F. Zhang, J. Wu, H.-Y. Zhang, J. Peng, C.-X. Liu, P. Wu, J.-X. Li, J. Org. Chem. 81 (2016) 1769.

[9] (a) H.C. Jeong, S.H. Lim, D.W. Cho, S.H. Kim, P.S. Mariano, Org. Biomol. Chem. 14 (2016) 10502;
(b) S.H. Lim, H.C. Jeong, Y. Sohn, Y.-I. Kim, D.W. Cho, H.-J. Woo, I.-S. Shin, U.C. Yoon, P.S. Mariano, J. Org. Chem. 81 (2016) 2460;
(c) S.H. Lim, D.W. Cho, P.S. Mariano, Heterocycles 93 (2016) 202.

[10] (a) S. Filippone, E.E. Maroto, A. Martin-Domenech, M. Suarez, N. Martin, Nat. Chem. 1 (2009) 578;
(b) E.E. Maroto, M. Izquierdo, S. Reboredo, J. Marco-Martinez, S. Filippone, N. Martin, Acc. Chem. Res. 47 (2014) 2660;
(c) E.E. Maroto, S. Filippone, M. Suarez, R. Martinez-Alvarez, A. de Cozar, F.P. Cossio, N. Martin, J. Am. Chem. Soc. 136 (2014) 705.

[11] (a) S.H. Lim, D.W. Cho, J. Choi, H. An, J.H. Shim, P.S. Mariano, Tetrahedron 73 (2017) 6249;
(b) S.H. Lim, J. Oh, K. Nahm, S. Noh, J.H. Shim, C. Kim, E. Kim, D.W. Cho, J. Org. Chem. 84 (2019) 1407.

[12] A. Padwa, Y.-Y. Chen, U. Chiacchio, W. Dent, Tetrahedron 41 (1985) 3529.

[13] (a) S.H. Lim, J. Yi, C.S. Ra, K. Nahm, D.W. Cho, G.Y. Lee, J. Kim, U.C. Yoon, P.S. Mariano, Tetrahedron Lett. 56 (2015) 3014;
(b) S.H. Lim, J. Yi, G.M. Moon, C.S. Ra, K. Nahm, D.W. Cho, K. Kim, T.G. Hyung, U. C. Yoon, G.Y. Lee, S. Kim, J. Kim, P.S. Mariano, J. Org. Chem. 79 (2014) 6946.

[14] M. Iyoda, F. Sultana, M. Komatsu, Chem. Lett. (1995) 1133.

[15] (a) J.W. Arbogast, A.O. Darmanyan, C.S. Foote, F.N. Diederich, R.L. Whetten, Y. Rubin, M.M. Alvarez, S.J. Anz, J. Phys. Chem. 95 (1991) 11;
(b) M. Terazima, N. Hirota, H. Shinohara, Y. Saito, J. Phys. Chem. 95 (1991) 9080.

[16] (a) X.M. Zang, S.-R. Yeh, S. Hong, M. Freccero, A. Albini, D.E. Falvey, P.S. Mariano, J. Am. Chem. Soc. 116 (1994) 4211;
(b) Z. Su, P.S. Mariano, D.E. Falvey, U.C. Yoon, S.W. Oh, J. Am. Chem. Soc. 120 (1998) 10676;
(c) D.W. Cho, U.C. Yoon, P.S. Mariano, Acc. Chem. Res. 44 (2011) 204.

[17] (a) R. Bernstein, C.S. Foote, Tetrahedron Lett. 39 (1998) 7051;
(b) R. Bernstein, C.S. Foote, J. Phys. Chem. A 103 (1999) 7244.

[18] (a) K.-F. Liou, C.-H. Cheng, Chem. Commun. (1996) 1423;
(b) L. Gan, J. Jiang, W. Zhang, S. Yang, Y. Shi, C. Huang, J. Pan, M. Lu, Y. Wu, J. Org. Chem. 63 (1998) 4240.

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