Reactions of C_{60} with α-Silylamine Derivatives: Two Types of [3+2] Addition of Azomethine Ylides to C_{60}

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(Received September 7, 1995)

Thermal [3+2] cycloaddition of C_{60} with α-silylamine derivatives proceeds smoothly under neutral conditions to afford fullerene-fused pyrrolidines and 1-pyrrolines in moderate to good yields. The new methods are effective for constructing fullerene derivatives containing bulky aryl-substituents.

Recently, a variety of cycloadditions of C_{60} have been reported whereby many fullerene derivatives have been synthesized.[1] In particular, the [3+2] cycloaddition is one of the most useful reactions for the construction of these fullerene derivatives. As has been reported previously, azomethine ylides have been frequently employed for the [3+2] cycloaddition reaction of C_{60} to give fullerene-fused pyrrolidines and 1-pyrrolines.[2]

Previously, one of us reported the reactions of (N-silylmethyl)imines and (N-silylmethyl)amides with ethylenes and acetylenes to give the corresponding [3+2] cycloadducts.[3] Interestingly, these reactions proceed smoothly under neutral conditions to give the [3+2] adducts in good yields. In order to develop a new method for the functionalization of C_{60}, we studied similar [3+2] cycloaddition reactions of C_{60} with (N-silylmethyl)imines and (N-silylmethyl)amides.

The reaction of C_{60} with N-(α-trimethylsilylbenzyl)-benzylideneamine (**1**) was first carried out (Scheme 1). Although the thermal reaction of **1** with olefins and acetylenes was reported to take place at 110-140 °C, the reaction of **1** with C_{60} required higher temperatures. Thus, a mixture of C_{60} (0.69 mmol) and **1** (0.69 mmol) in dry toluene (10 ml) was heated in a sealed tube at 160 °C for 24 h. The products were separated by column chromatography on silica gel to give a single isomer of the 1:1 adduct **2** (33%) and a mixture of the regioisomers of the 1:2 adducts **3** (6.5%) with the recovered C_{60} (60%).[4] Taking into account the yield of the recovered C_{60}, the yields of **2** and **3** are raised to 83% and 16%, respectively. Therefore, it can be concluded that the [3+2] cycloaddition of C_{60} with the azomethine ylide **4** (Ar = Ph) proceeds smoothly to give the adducts in good yields. The structure of the 1:1 adduct **2** was assigned as a trans-1,3-diphenyl form on the basis of the spectroscopic analysis and the expected reaction mechanism. An attempted separation of the regioisomers of the 1:2 adducts **3** was unsuccessful, and the addition of **4** to **2** shows no clear selectivity.

N-(α-Trimethylsilylbenzyl)benzylideneamines can be easily prepared by the condensation of aldehydes with α-silylated benzylamines. Thus, the imine **5** was prepared from 2,5-dimethoxybenzaldehyde and α-trimethylsilylbenzylamine in a quantitative yield. The thermal reaction of C_{60} with **5** [toluene, 200 °C, 20 h, in a sealed tube] gave the 1:1 adduct **6** (62% based on the consumed C_{60}) and a mixture of the 1:2 adduct **7** (15% based on the consumed C_{60}) with the recovered C_{60} (53%). These results show that the reaction of C_{60} with α-silylated benzylamine can be applied for the construction of bulky aryl-substituted fullerene derivatives.

Next we tried the thermal reaction of C_{60} with (N-silylmethyl)amides **8** (Scheme 1). Since **8** produces the azomethine ylide **9** upon heating, the reaction of C_{60} with **8** can be expected to lead to a new type of fullerene derivatives. The reaction of C_{60} with 1 equiv. of **8** in toluene proceeded at 160-180 °C for 24 h to afford the two 1:1 adducts **10**[5] (39%) and **12** (11%) and a mixture of the 1:2 adduct **11** (25%). The adduct **12** was obtained as a mixture of two configurational isomers. The formation of 1-pyrroline derivatives **10** and **11** can be explained by the [3+2] cycloaddition of **9** to C_{60}, followed by elimination of trimethylsilanol from the adduct.

In order to examine the redox behavior of the new fullerenes, the reduction potentials of C_{60}, **2**, **6**, and **10** were measured by cyclic voltammetry (Table 1). All compounds show reversible three one-electron reductions corresponding to monoanion radicals, dianions, and trianion radicals. Usually, dialkyl-substitution on the 6:6 bond of C_{60} causes the first reduction potentials to shift negative by 0.1 V.[6] In agreement with this observation, the first reduction potential of **2** shifts negative by 0.14 V relative to C_{60}. Interestingly, the first reduction potential of **6** having 2,5-dimethoxy substituent shifts negative by 0.03 V as compared to **2**, due to the weak donor-acceptor interaction between the 2,5-dimethoxyphenyl group and fullerene moiety.[7] On the contrary, the first reduction potential of **10** shifts positive by 0.05 V as compared to **2**. This positive shift may be attributable to the effect of the electron-withdrawing C=N double bond in the 1-pyrroline ring of **10**.

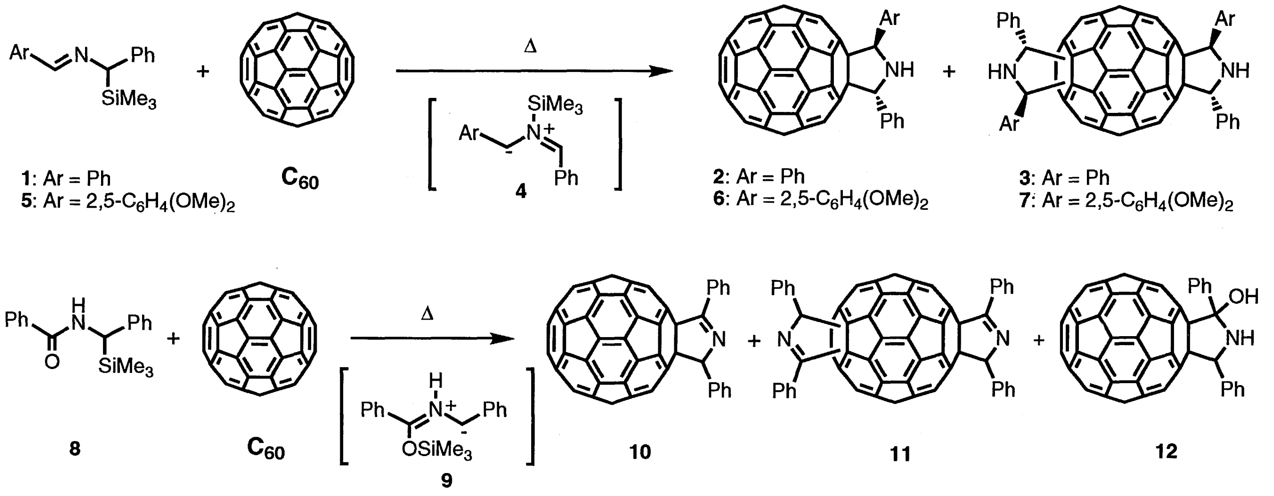
Table 1. Cyclic voltammetric data of fullerenes[a]

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	$E^3_{1/2}$/V
C_{60}	-1.09	-1.52	-2.00
2	-1.23	-1.62	-2.15
6	-1.26	-1.64	-2.18
10	-1.18	-1.57	-2.09

[a]Conditions: n-Bu_4NPF_6 (0.05 mol dm^{-3}), 1,2-dichlorobenzene, 25 °C, glassy carbon working and Pt counter electrodes, 100 mV s^{-1}. Potentials were measured vs Fc/Fc^+ using Ag/Ag^+ reference electrode.

In summary, our new methods reported here have been successfully applied for the synthesis of fullerenes containing donor (2,5-dimethoxyphenyl group) and acceptor (C_{60}) moieties. Furthermore, new fullerene-fused 1-pyrrolines have been synthesized using the thermal reaction of C_{60} with (N-silylmethyl)amides.

We thank Drs. M. Yoshida, S. Sasaki, and H. Matsuyama, Tokyo Metropolitan University for helpful discussions. Financial



Scheme 1.

support by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan (06227257 and 06224223) is gratefully acknowledged.

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4 The structures of all new compounds reported here were fully characterized by the spectroscopic analysis. The selected data are as follows. **2**: black fine crystals, mp 300 °C (decomp); FAB-MS (*m/z*) 915 (M^+); ^1H NMR (CD_2Cl_2) δ 3.55 (t, J = 4.5 Hz, 1H, NH), 6.49 (d, J = 4.5 Hz, 2H, CH), 7.38 (t, J = 7.5 Hz, 2H, *p*-Ph), 7.49 (t, J = 7.5 Hz, 4H, *m*-Ph), 7.94 (d, J = 7.5 Hz, 4H, *o*-Ph); ^{13}C NMR (CD_2Cl_2-CS_2) δ 156.51, 153.56, 147.62, 147.53, 146.81, 146.61, 146.52, 146.36, 145.95, 145.75, 145.68, 145.55, 144.97, 144.75, 143.52, 143.01, 142.66, 142.57, 142.52, 142.19, 140.54, 140.47, 140.06, 137.18, 137.03, 135.80, 129.48 (Ph), 129.24 (p-Ph), 128.73 (o,m-Ph), 128.54, 77.85 (C_{60}-sp^3), 74.92 (CH); UV-vis (C_6H_{12}) λmax (ε) 256 (63900), 310 (22100), 430 (1830), 634 (183), 701 (183). **6**: black crystals, mp 280-290 °C (decomp.); MS (*m/z*) 976 (M^++1); ^1H NMR ($CDCl_3$) δ 3.53 (brs, 1H, NH), 3.74 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.00 (d, J = 4.4 Hz, 1H, CH), 6.44 (d, J = 4.4, 1H, CH), 6.86 (m, 2H, Ar), 7.37 (t, J = 7.5, 1H, *p*-Ph), 7.46 (t, J = 7.5, 2H, *m*-Ph), 7.88 (d, J = 2.9, 1H, Ar), 7.99 (d, J = 7.5, 2H, *o*-Ph). **10**: black crystals, mp 350-360 °C (decomp.); FAB-MS (*m/z*) 913 (M^+); ^1H NMR (CD_2Cl_2) δ 7.21 (s, 1H, CH), 7.40 (m, 1H, *p*-Ph-CH), 7.50 (m, 2H, *m*-Ph-CH), 7.55-7.59 (m, 3H, *p*- and *o*-Ph-C=N), 7.76 (m, 2H, *o*-Ph-CH), 8.24 (m, 2H, *o*-Ph-C=N); ^{13}C NMR (CD_2Cl_2-CS_2) δ 171.04 (C=N), 155.63, 153.07, 149.19, 148.11, 147.62, 147.36, 146.98, 146.78, 146.72, 146.39, 146.30, 146.19, 146.10, 146.01, 145.92, 145.77, 145.62, 145.50, 145.41, 145.31, 144.84, 144.75, 144.45, 143.58, 143.17, 143.12, 143.05, 142.94, 142.68, 142.59, 142.44, 142.39, 142.30, 142.20, 142.15, 142.06, 140.94, 140.54, 140.23, 136.68 (40 peaks of C_{60}-sp^2), 135.31, 135.02 (2 peaks of Ph), 134.32 (C_{60}-sp^2), 130.99 (*p*-Ph), 129.73, 129.40, 129.09 (3 peaks of *o*- or *m*-Ph), 128.80 (*p*-Ph), 128.67 (*o*- or *m*-Ph), 88.80, 88.69, 78.21 (C_{60}-sp^3 and CH).

5 The diphenylpyrroline derivative **10** has been prepared by [3+2] photocycloaddition of C_{60} with 2,3-diphenyl-*2H*-azirine: J. Averdung, E. Albrecht, J. Lauterwein, H. Luftmann, J. Mattay, H. Mohn, W. H. Müller, and H.-U. ter Meer, *Chem. Ber.*, **127**, 787 (1994).

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