



The Reaction of [60]Fullerene with Lithium Fluorenyl: Formation of a Novel 1,4-Adduct of [60]Fullerene

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Abstract: Reaction of fullerene C₆₀ in THF with lithium fluorenyl afforded 1-fluorenyl-1,2-dihydro[60]fullerene **2** after protonation. When the reaction time was extended to 24 h, an unusual adduct **3** was obtained, which had two fluorenyl groups attached at the 1,4-positions of a six-membered ring of C₆₀. The structure of **3** was confirmed by comparison of its properties with those of corresponding trimethylene-bridged adduct **5**. Copyright © 1996 Elsevier Science Ltd

The addition of carbon nucleophiles is one of the versatile methods for functionalization of fullerene C₆₀.^{1,2} So far there have been reactions reported such as the addition of organolithium and Grignard reagents of alkyl,³⁻⁵ phenyl,^{3b} and alkynyl groups^{6,7} and sodium cyanide.⁸ These nucleophilic reactions are advantageous because the monoaddition products are selectively obtained in fairly good yields under mild conditions and two different organic groups can be introduced into C₆₀ by treatment of the first formed anion RC₆₀⁻ with various electrophiles.^{6b, 7b, 8, 9}

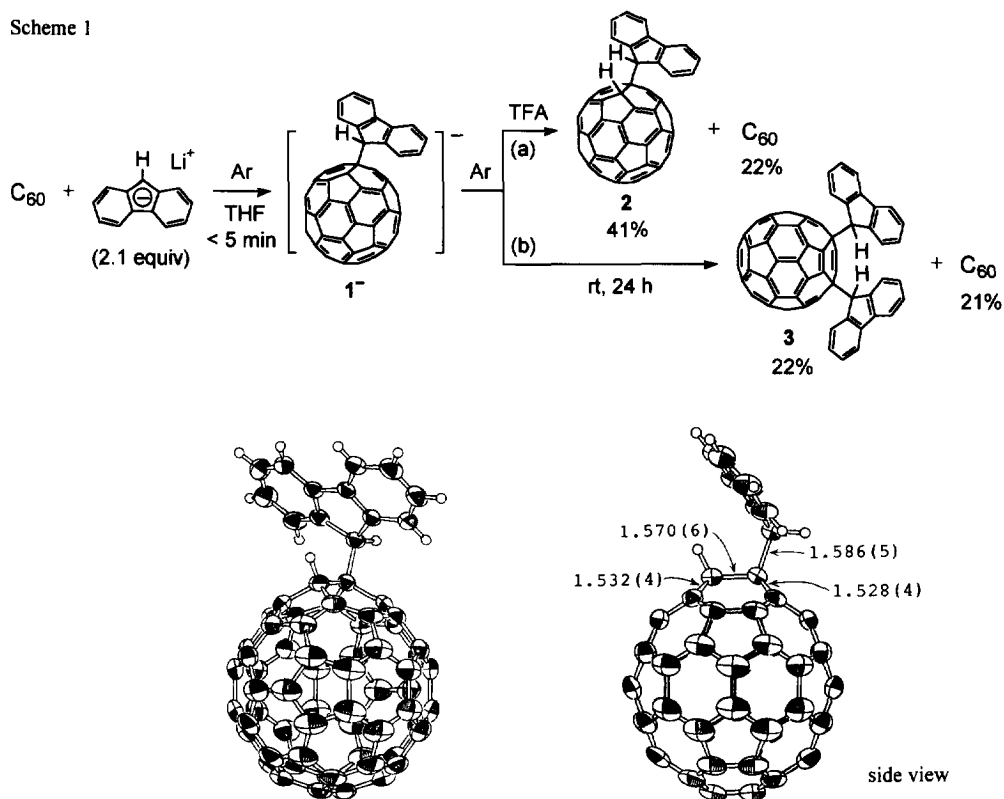
A C₆₀ derivative having cyclopentadiene moiety, together with an alkyl group in place of acidic hydrogen, could be a good precursor for a cyclopentadienide-connected C₆₀. However, to the best of our knowledge, there is no report on the reaction of C₆₀ with cyclopentadienide and related carbanions. In our attempt to prepare a fluorenyl-substituted dihydrofullerene, we found that either a monoadduct or an anomalous 1,4-bisadduct⁵ can be formed by simply changing the reaction time, as is reported below.

As shown in Scheme 1, a THF solution of lithium fluorenyl (0.33 mmol) was slowly added to a vigorously stirred suspension of C₆₀ (0.153 mmol) in THF (50 ml) at room temperature under argon to afford immediately a dark green^{6b} suspension of anion 1⁻. Acidification of this suspension with trifluoroacetic acid (Scheme 1 (a)) gave a dark brown suspension, from which was isolated monosubstituted dihydrofullerene **2** in 41% yield as a brown powder along with 22% yield of C₆₀.

The 1,2-dihydrofullerene structure with C_s symmetry was assigned to **2** based on spectral data.¹⁰ Furthermore, the X-ray structure was determined for a single crystal of 2·2C₆H₆, grown from the benzene solution, as shown in Fig. 1.¹¹ This is the first X-ray structure of a monosubstituted dihydro[60]fullerene. In addition to selected bond lengths given in the figure, it is noted that bond lengths of the 6,6-bond are in the range between 1.354(6) and 1.403(5) Å, and those of 5,6-bond are between 1.418(4) and 1.461(8) Å, in agreement with the reported values.¹²

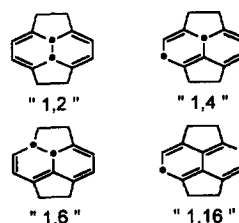
When the initially formed dark green suspension of the fluorenyl-C₆₀ anion 1⁻ was stirred at room temperature for 24 h the mixture slowly changed its color to dark brown, and after evaporation, a totally new adduct with a highly symmetrical structure, i.e. 1,4-bisadduct **3**, was isolated in 22% yield as a brown powder (Scheme 1(b)). In addition to C₆₀, which was recovered in 21% yield, there was obtained a large amount of highly insoluble material.

Scheme 1

Fig. 1. X-ray structure of 2·2C₆H₆. Benzene molecules are omitted for clarity.

The structure of 3 having a C₃ symmetry with two fluorenyl groups attached at the 1,4-positions of a six membered ring of C₆₀ was determined based on spectral and analytical data.¹³ The DCI mass spectrum displayed peaks at m/z 1050 (M⁻, 14%), 885 (M⁻-C₁₃H₉, 19%), and at 720 (M⁻-C₂₆H₁₈, 100%). The ¹³C NMR spectrum supports the structure 3 by exhibiting 8 signals (with one signal overlapped) for sp²-CH in fluorenyl groups, 4+31 signals (with three signals overlapped) for fully substituted sp²-C in fluorenyl and C₆₀ moieties, and 2 signals for sp³-C. The ¹H NMR spectrum, which also supports the structure 3, exhibited considerable broadening, suggesting the presence of some dynamic behaviors.¹⁴ A dilute solution of 3 in cyclohexane was yellow in color instead of brown, which is commonly observed for 1,2-dihydrofullerenes, and its UV-vis spectrum exhibited a characteristic absorption pattern, i.e. a rather broad absorption at 443 nm, which appears to be typical for the 1,4-dihydrofullerenes,¹⁵ instead of a sharp peak around 430 nm diagnostic of 1,2-dihydrofullerenes.

In order to confirm the structure of 3 as a 1,4-adduct, we conducted a reaction of C₆₀ with trimethylenebisfluorenyl dianion (4²⁻). Inspection of the molecular model indicates that, among the modes of addition in a pyracylene framework, addition at "1,4 positions"¹⁶ would give the most stable structural isomer because of the presence of a trimethylene bridge. As shown in Scheme 2, the reaction conducted under the same conditions as in Scheme 1(b) afforded an adduct. Close resemblance of the spectral properties of this adduct¹⁷ to those of 3 suggests its structure to be 1,4-bisadduct 5, which is quite similar to that of 3.



This is also supported by the similarity in the optimized structures of **3** and **5** obtained by AM1 calculations as shown in Fig. 2.

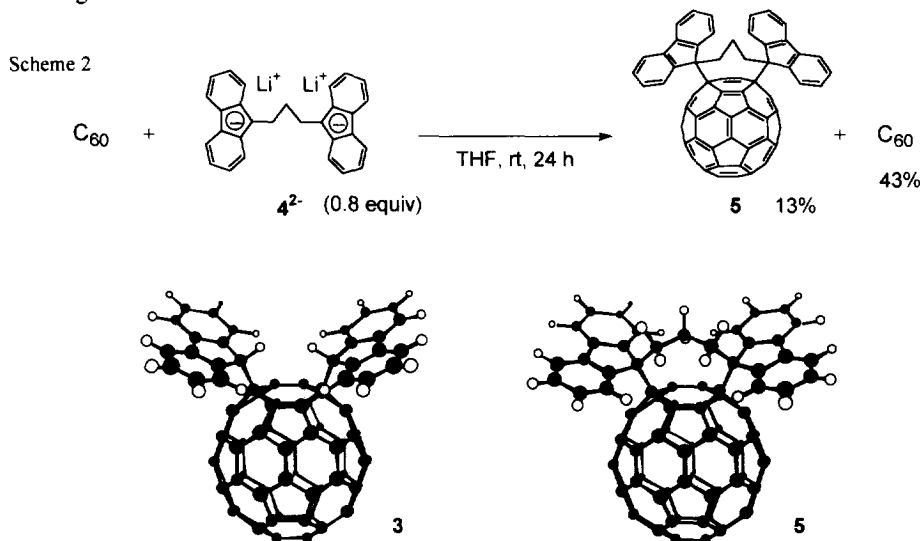
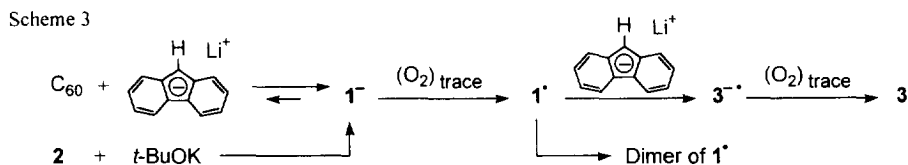


Fig. 2. The optimized structures of **3** and **5** obtained by AM1 calculations.

Control experiments gave the following results. (i) Fluorenyl- C_{60} anion **1**⁻ was generated from **2** and *t*-BuOK in THF under argon using a rubber balloon as in the case of the reaction of Scheme 1(b) and was stirred for 15 h. From the resulting dark brown suspension, adduct **3** and C_{60} were isolated in 13% and 21% yields respectively. (ii) The introduction of dry air into the suspension of **1**⁻ resulted in the immediate disappearance of the green color of **1**⁻ and the formation of **3** (8%) together with a large amount of insoluble material which could be the dimer of **1**[•].¹⁸ (iii) The reaction of C_{60} and lithium fluorenyl conducted under high vacuum ($\sim 10^{-5}$ mmHg) for 5 days at room temperature did not afford **3**. Most of the starting materials were recovered. From these results, a possible mechanism for the formation of adduct **3** can be considered as follows (Scheme 3). The reaction should start from fluorenyl- C_{60} anion **1**⁻, which would be slowly oxidized to the corresponding radical **1**[•] by a trace amount of oxygen. Some amount of radical **1**[•] would undergo dimerization, but the rest of **1**[•] could react with the fluorenyl ion to give radical anion **3**^{-•}, which could be oxidized again to furnish adduct **3**.



Further studies are now in progress to clarify the dynamic NMR behavior in **3** and also to investigate the occurrence of similar reactions with other carbanions.

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- 2: brown powder, mp > 300 °C; MS (+APCI): m/z 886 [M^+], 720 [$M^+-C_{13}H_9$]; 1H NMR (300 MHz, CS_2 -acetone- d_6 (7:1)): δ 8.33 (d, $J = 7.6$, 2H), 8.07 (d, $J = 7.3$, 2H), 7.64 (m, 2H), 7.54 (m, 2H), 5.59 (s, 1H), 5.34 (s, 1H); ^{13}C NMR (75.4 MHz, CS_2 -acetone- d_6 (7:1)): δ 154.81, 154.55, 147.30, 147.04, 146.66, 146.26, 146.17, 146.03, 146.00, 145.96, 145.53, 145.50, 145.25, 145.19, 145.12, 144.59, 144.35, 143.15, 142.81, 142.39, 142.34, 142.11, 142.08, 141.81, 141.53, 141.27, 141.18, 139.94, 139.89, 137.64, 135.98, 129.02, 127.76, 127.27, 120.47, 67.50, 57.89, 55.08; UV-Vis (C_6H_{12}): λ_{max} 212 nm (log ϵ 5.73), 257 (5.07), 309 (4.54), 407 (3.62), 434 (3.54), 642 (2.51), 675 (2.19), 697 (2.42), 709 (2.59). Anal. Calcd for $C_{73}H_{10}$: C, 98.86; H, 1.14. Found: C, 98.62; H, 1.23.
- Crystallographic data for 2· $2C_6H_6$ at 293 K: monoclinic, $P2_1/m$, $Z = 2$; $a = 10.158(2)$ Å, $b = 18.931(1)$ Å, $c = 12.852(1)$ Å, $\beta = 113.111(8)^\circ$, $V = 2279.2(5)$ Å³, $d_{calc} = 1.520$ g/cm³, 2θ range = 20.6–48.0°, Cu K α , $\lambda = 1.54178$ Å, 3745 reflections, 3526 independent; solution: direct method (MULTAN-88), $R = 0.049$, $R_w = 0.052$, GOF = 1.82, 1993 reflections with $I > 3.0\sigma(I)$. Further details are deposited with the Cambridge Crystallographic Data Centre.
- For example of a 1,2-bisadduct, see Ref. 8. For example of a Diels-Alder adduct, see Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretizian, C. *J. Am. Chem. Soc.* 1993, 115, 344-345.
- 3: brown powder, mp > 300 °C; MS (-DCI): m/z 1050 [M^-], 885 [$M^- - C_{13}H_9$], 720 [$M^- - C_{26}H_{18}$]; 1H NMR (300 MHz, CS_2 -acetone- d_6 (7:1)): δ 7.98 (m, 4H), 7.75 (m, 4H), 7.32 (m, 8H), 4.53 (br, s, 2H); ^{13}C NMR (75.4 MHz, CS_2 -acetone- d_6 (7:1)): δ 154.81, 150.62, 148.57, 148.35, 147.36, 146.85, 146.67, 146.63, 145.95, 145.29, 145.24, 144.85, 144.39, 144.14, 144.03, 143.96, 143.85, 143.64, 143.05, 143.02, 142.98, 142.85, 142.63, 142.39, 142.31, 142.10, 141.84, 141.72, 141.24, 140.14, 138.88, 138.42, 128.48, 128.30, 127.43, 126.58, 126.54, 120.41, 120.19, 61.56, 56.86; UV-Vis (C_6H_{12}): λ_{max} 210 nm (log ϵ 5.30), 258 (5.08), 325 (4.45), 443 (3.76), 553 (3.07), 685 (2.34). Anal. Calcd for $C_{86}H_{18}$: C, 98.27; H, 1.73. Found: C, 98.11; H, 1.72.
- This is supposed to be due to hindered rotation of the fluorenyl groups. The results of preliminary studies on variable-temperature NMR indicate that the energy barrier for this rotation is nearly 12 kcal/mol. Results of the more detailed studies will be reported elsewhere.
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- For the numbering system, see Taylor, R. *J. Chem. Soc., Perkin. Trans. 2* 1993, 813-824.
- 5: brown powder, mp > 300 °C; MS (-DCI): m/z 926 [$M^- - C_{13}H_9$], 720 [$M^- - C_{29}H_{22}$]; 1H NMR (300 MHz, CS_2 -acetone- d_6 (7:1)): δ 8.33 (m, 2H), 7.96 (m, 2H), 7.72 (m, 4H), 7.40 (m, 8H), 4.09 (br, d, $J = 15$, 1H), 3.27 (dd, $J = 15$, 4.5, 2H), 2.67 (dt, $J = 13$, 2.3, 2H), 2.54 (br, t, $J = 13$, 1H); ^{13}C NMR (75.4 MHz, CS_2 -acetone- d_6 (7:1)): δ 156.45, 149.83, 149.00, 148.91, 148.33, 147.26, 146.89, 146.71, 146.62, 145.82, 145.44, 145.26, 144.65, 144.28, 144.08, 143.94, 143.82, 143.62, 143.34, 142.99, 142.91, 142.83, 142.70, 142.65, 142.30, 142.23, 142.16, 141.94, 141.81, 141.37, 141.01, 139.93, 139.53, 139.24, 138.00, 128.61, 128.25, 127.42, 126.82, 126.63, 125.64, 120.48, 120.11, 64.69, 61.01, 43.12, 16.87; UV-Vis (C_6H_{12}): λ_{max} 211 nm (log ϵ 5.39), 258 (5.19), 329 (4.60), 447 (3.85), 702 (2.75). Anal. Calcd for $C_{89}H_{22}$: C, 97.97; H, 2.03. Found: C, 97.64; H, 2.04.
- Oxidation with iodine gave the same results. For the dimerization of *t*-BuC₆₀ radical, see Ref. 4.