A novel migrative addition reaction of hydrazines to the diketone derivative of C60†

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A novel addition reaction of an aromatic hydrazine to the diketone derivative of C60 occurs highly regioselectively with an unusual migration of two hydrogen atoms from the hydrazine to the fullerene and affords a fluorescent product having a methylene carbon along the orifice.

Surface modification of fullerenes has been developed dramatically in the last decade;[1] however, the introduction of two or more molecular units onto fullerene has still remained a challenge because of poor regioselectivity.[2] Although the reversible template method and the tether-directed method has succeeded for constructing multiple adducts in a regioselective manner,[3,4] some limitations are pointed out especially from the viewpoint of reaction efficiency and variety of molecular design.

Recently, we found that bis(fulleroid),[5–8] prepared by the reaction of the palladacyclopentadiene with C60 followed by photochemical rearrangement,[8] was easily oxidized under photo irradiation to afford the diketone derivative **1** in quantitative yield.[9] Compound **1** has a 12-membered ring on the C60 surface, and such a ring-opened derivative has been expected to be a key starting material for the synthesis of endohedral fullerenes.[10] From a different perspective we have been interested in the characteristic reactivity of **1** based on the α,β-unsaturated carbonyl structure for efficient construction of a multiple adduct in a regioselective manner. Herein, we describe the regioselective addition reaction of an aromatic hydrazine to **1**.[11]

The addition reaction of **1** with phenylhydrazine (**2a**) proceeded at room temperature in toluene (Scheme 1).[12] The reaction was not particularly sensitive to moisture or atmospheric oxygen, and even in the presence of an excess of **2a** (5 equiv.), only the single product was recognized in the crude ^{1}H NMR spectrum. After purification by silica-gel chromatography, **3a** was obtained in 81% yield as a reddish brown solid. The reaction was characteristic of the diketone **1**, and a similar reaction did not proceed when bis(fulleroid) was employed as a starting material instead of **1**.
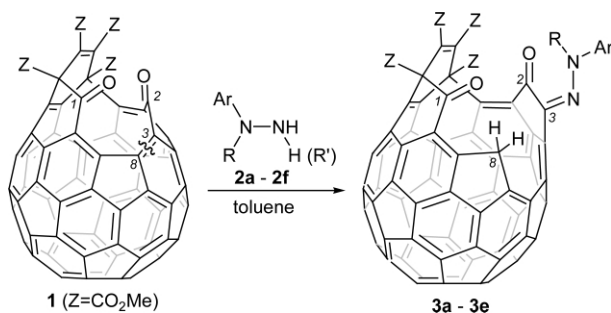
Scheme 1 Reaction of **1** with an aromatic hydrazine. Atom numbers shown in the structures correspond to Fig. 2.

It made sense that a simple hydrazone-forming substitution or a conjugate Michael-type addition occurred in the reaction of **1** with phenylhydrazine. Indeed, the ES-mass spectrum (negative) of **3a** showed a molecular ion peak at m/z 1144 indicating that the product was the 1 : 1 adduct without elimination of water by forming a hydrazone. However, subsequent ^{1}H and ^{13}C NMR studies contradicted the simple 1,4-adduct structure. In the ^{1}H NMR spectrum, a pair of doublets was observed at δ 5.30 and 4.73 ppm (each 1H, J = 20 Hz) together with a labile proton at δ 13.86 ppm, which disappeared on treatment with D_2O. In the ^{13}C NMR spectrum, two carbonyl signals assignable to ketones were observed respectively at δ 190.52 and 185.61 ppm (192.06 and 189.59 ppm in **1** respectively), and the two quaternary sp3 signals characteristic of the fulleroid bridge carbons (δ 63.86 and 55.86 ppm) were also observed in regions similar to **1**. These results indicated that the structure of the exohedral moiety of **1** was basically retained. In accordance with a couple of geminal protons observed in the ^{1}H NMR, one methylene carbon which was confirmed by DEPT135 and HMQC spectra was observed at 43.80 ppm. The IR spectrum showed three peaks characteristic of the product **3a** at ν 1686, 1537 and 1478 cm^{-1} in addition to similar peaks observed for **1**. The visible region of the UV/Vis spectrum of **3a** was completely different from that of **1**, reflecting the color of the solution, and showed diagnostic absorptions at λ 438, 536 and 681 nm. In addition, a significant fluorescence on **3a** was observed at 720 nm (excited at 540 nm) as shown in Fig. 1.

In order to confirm the structure, we prepared ^{13}C-enriched **3a** from ^{13}C-enriched (10–15%) C60, and its partial structure (**s-3a**) was assigned as follows (Fig. 2a): Selective INADEQUATE NMR experiments at the signals of δ 186.2 and 190.9 ppm for the enriched **3a** in C_6D_6 showed that the former carbon was connected to two sp2 carbons at δ 135.9 [C(3)] and 136.5 ppm [C(4)] (J_{CC} = 54 and 56 Hz, respectively) and that the latter was connected to only one signal at δ 128.7 ppm [C(5)] (J_{CC} = 57 Hz). In the ^{13}C-enriched **1**, the ketone carbon [C(2) in Scheme 1] was connected to two enriched neighboring carbons, whereas C(1) was connected to only one enriched carbon because the neighboring sp3 carbon was derived by surface modification of C60. Thus, two ketone signals at δ 186.2 and 190.9 ppm of **3a** were assigned as C(2) and C(1), respectively. The same measurement for the methylene carbon observed at δ
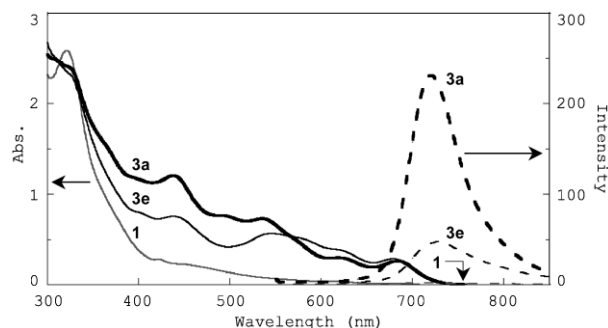

Fig. 1 UV/Vis (solid lines) and fluorescence spectra (excited at 540 nm, broken lines) of **1**, **3a** and **3e** (5.8–6.0 × 10^{-5} M CH$_2$Cl$_2$ solution).

Table 1 Reaction of diketone **1** with **2a–e**[a]

Entry	Hydrazine	Ar	R	R′	T/°C	t/h	Product	Yield (%)
1	**2a**	C_6H_5	H	H	r.t.	4	**3a**	81
2[b]	**2b**	$2,4\text{-}(NO_2)_2C_6H_3$	H	H	100	4	**3b**	50
3[b]	**2c**·HCl	4-MeOC_6H_4	H	H	60	8	**3c**	85
4[b]	**2d**·HCl	4-BrC_6H_4	H	H	60	8	**3d**	89
5	**2e**	C_6H_5	Ph	H	60	8	**3e**	85
6	**2f**	C_6H_5	H	Ph	80	3	—	N.R.[c]

[a] 5 equiv. hydrazines were used. [b] Pyridine (2 equiv. relative to hydrazine) was added as a base. [c] N.R. = no reaction.
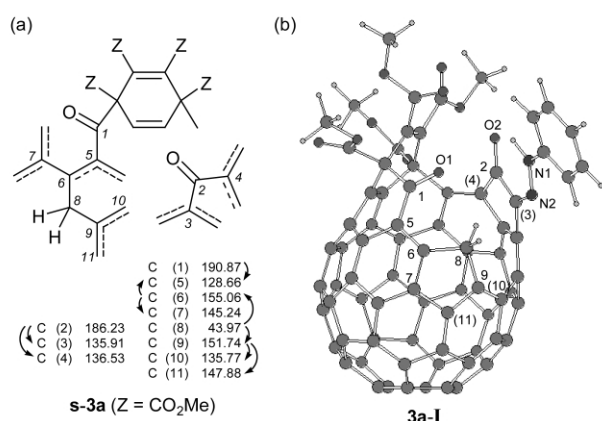

Fig. 2 (a) Partial structure of **s-3a** assigned by selective INADEQUATE 1D and HMBC measurements. (b) The possible structure **3a-I** optimized at the B3LYP 6-31G(d) level. Atom positions of C(3), C(4), C(10) and C(11) are not fully assigned.

44.0 ppm [C(8)] showed the relationship to two sp² carbons at δ 155.1 [C(6)] and 151.7 ppm [C(9)] (J_{CC} = 41 and 40 Hz, respectively).[13] In a similar way, C(6) was connected to two sp² carbons at δ 128.7 ppm already assigned as C(5) and at δ 145.2 ppm [C(7)]. For C(9), two carbons at δ 135.8 [C(10)] and 147.9 ppm [C(11)] were observed.[14] From these results, we concluded that the product **3a** has **s-3a** as the partial structure.

There are three candidates satisfying the structure of **s-3a**. One of these (**3a-I**) has a hydrazone structure with a methylene carbon by the bond breaking of C(3)–C(8) as shown in Fig. 2b, and the other two require N–N bond cleavage of the hydrazine employed.[15] Thus, in order to confirm the existence of the N–N bond in the product, we prepared ¹⁵N-enriched **3b** by the reaction with ¹⁵N-enriched 2,4-dinitrophenylhydrazine (Ar¹⁵NH¹⁵NH₂, 99% ¹⁵N for each atom).[16] In the ¹⁵N NMR spectrum of the enriched **3b**, two peaks were observed at δ 301 and 126 ppm with J_{NN} = 12 Hz, supporting the idea that the N–N bond exists in the product. Further, the downfield chemical shift of the labile NH proton observed in the ¹H NMR and the characteristic IR absorptions of **3a** quite resemble those of acenaphthenequinone monophenylhydrazone (Fig. 2b).[17] Thus, we concluded that the most plausible structure is **3a-I**.

Reactions of 4-methoxy- and 4-bromo-phenylhydrazine hydrochlorides afforded **3c** and **3d** in 85 and 89% yields, respectively (entries 3 and 4, Table 1). The reaction of 1,1-diphenylhydrazine afforded the corresponding product **3e** in 85% yield (entry 5). The NH₂ moiety was essential to carry out the reaction. The reaction with 1,2-diphenyhydazine resulted in complete recovery of **1** (entry 6). Aliphatic 1,1-dimethylhydrazine initially afforded the corresponding compound by ¹H NMR and ES-MS (neg.) analyses, but isolation of the product has not been successful because the product immediately rearranged to another structure. Identification of the rearranged product is now underway. The reaction with methylhydrazine was too sluggish to analyze.

In summary, we have demonstrated that the addition reactions of the diketone derivative of C_{60} with aromatic hydrazines proceed highly regioselectively and afford unusual addition products having methylene carbons on the C_{60} surface. The reaction is characteristic of the diketone structure. Further investigations on the crystallographic structural analysis, reaction mechanism and applications are now in progress.

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