Unusual Products of Enamines with [60]Fullerene

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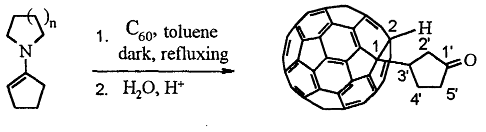
Unusual products were isolated from reactions of [60]fullerene with cyclopentenyl or cyclohexenyl pyrrolidine and piperidine. The structures of products were characterized by spectroscopic means. A possible thermoinduced electron-transfer mechanism for the new reaction was proposed.

It is well known that enamines react with electron-deficient olefins to give α-substituted ketones[1] *via* nucleophilic addition process. Because the 6-6 double bonds of the [60]fullerene beheave like electron-deficient olefins,[2] we wished to extend these reactions to [60]fullerene. In the course of our research we found that [60]fullerene reacted with enamines **1** in the dark unexpectedly to form 1-(β-ketocyclopentyl)-1,2-dihydro-[60]fullerene **2** (Scheme 1), not the expected α-isomer of usual nucleophilic addition. Herein, we wish to report our preliminary results of this new reaction and the characterization of the unusual product **2**.



1 **2**

a: n=1, conversion: 70%, yield: 6%
b: n=2, conversion: 52%, yield: 27%

Scheme 1.

The reactions were conducted in the dark in order to exclude the possible interference of the photoinduced reactions, since there have already been a number of examples of photoinduced radical reactions of [60]fullerene with amines especially tertiary amines.[3] Typically, 0.05 mmol of [60]fullerene was allowed to react with excesses of **1** (5 eqv. for **1a** and 12 eqv. for **1b**) in 20 ml toluene under heating till the color of the mixture changed from purple to brown. Upon hydrolysis, the major product **2** was formed, then isolated and purified by flash chromatography on silica gel.

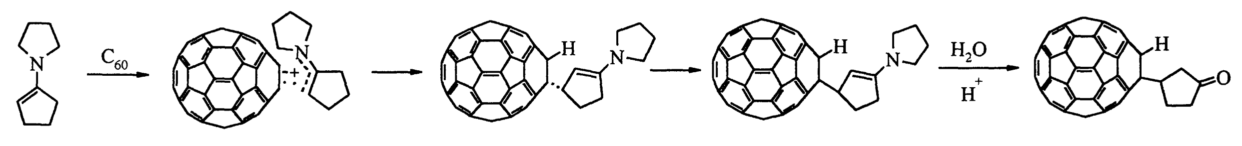
The structure of **2** was fully characterized by means of spectroscopies including MS, ^{1}H NMR, ^{13}C NMR, HMQC, HMBC, ^{1}H-^{1}H COSY, UV-Vis and FT-IR.[4] On the basis of known chemistry of [60]fullerene[2] and the data of ^{13}C NMR (the signals of two sp^3-carbons of the cage at 59.13 and 67.91 ppm) and UV-Vis (the band at 430 nm),[5] it is reasonable to believe that the reactions occurred at the [6,6] ring junction of [60]fullerene framework.

At first, we considered the product to be the expected normal nucleophilic adduct, for the routine spectral analysis (TOF-SIMS, ^{13}C NMR and ^{1}H NMR) well demonstrated that a ketocyclopentyl and a proton had attached to the fullerene cage. What brought to our attention was that the signal of the methine proton at δ 4.27 ppm in the ^{1}H NMR spectrum appeared as a multiplet, not as the *dd* coupling pattern as we predicted. This suggested that such proton should be the β methine proton in the structure of **2**, rather than the α one in the assumed product. It was clear when the 2D NMR experiments were carried out. The HMQC and ^{1}H-^{1}H COSY spectra unambiguously established the moiety of $CH_2CHCH_2CH_2$, which confirmed the structure of **2**. Moreover, the junction of C-1 and C-3' was proven by the HMBC spectrum in which both the H-2' and H-4' showed obvious three-bond crosspeaks with C-1.

For this unusual reaction, using the known mechanism of reactions of [60]fullerene with tertiary amines as reference[3], a likely thermoinduced electron-transfer radical mechanism was proposed (with the supporting of ESR studies)[6] as described as follows (Scheme 2). The reaction started with the electron-transfer from enamine to fullerene forming a delocalized enamine-fullerene radicals ion pair **3**. Then **3** changed to fullerene allylic enamine radical pairs **4** *via* allylic deprotonation. Subsequent combination of the radical pair led to fullerene-enamine **5**, which gives **2** after hydrolyzing.

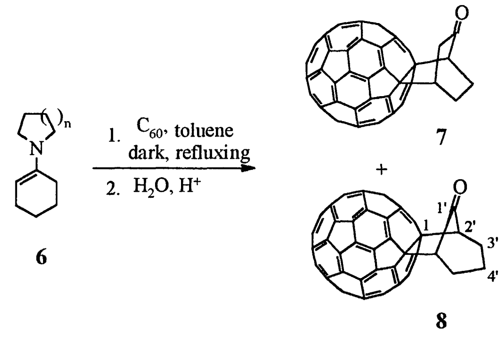
In order to expand the scope of this kind of new reaction, the reactions of [60]fullerene with enamines **6** were studied (Scheme 3) under the similar conditions as above. However they seem a little more complicated than the former. Two interesting fullerene fused bicyclooctanones **7** and **8**, as well as a mixture of two inseparable components (by chromatography on silica gel) were isolated.

Compound **7** was a known substance once prepared by Rubin and Takeshita respectively from [60]fullerene and 2-cyclohexenone *via* sequential double-Michael addition of dienolate[7] and Diels-Alder reaction.[8] In our case, the structure of **7** was confirmed by spectral analysis of HMQC and HMBC



1 **3** **4** **5** **2**

Scheme 2.



a: n=1, conversion: 60%, yield: **7**: 12%, **8**: 13%
b:n=2, conversion: 68%, yield: **7**: 7%, **8**: 6%

Scheme 3.

and by comparing the ^{1}H NMR and ^{13}C NMR spectra with those from Rubin. The structure of the new [60]fullerene fused bicyclooctanone **8** was elucidated by the combination of spectroscopic methods.[9] Still, the 2D NMR analysis provided the key messages for establishing the structure, such as the locations of protons to their carbons from HMQC, the connectivities of carbons from ^{1}H-^{1}H COSY and the long range correlations of the side ring protons with the fullerene sp^3-carbons from HMBC *etc.*.

We have no definitive answers so far whether one of the products in the inseparable mixture of reactions **6** was the desired analogue of **2**, though some information from the spectral analysis of the mixture, such as the M$^+$ peak at *m/z* 818 ($C_{66}H_{10}O$), the strong carbonyl absorption at 1740 cm^{-1} and the typical ^{1}H NMR absorption of C_{60}-H at δ 6.51 ppm, *etc.* suggested that an analogue of **2** may also formed.

Studies on the reaction mechanism for the formation of products **7** and **8**, and on the methods of separating the mixture in the second reaction are in progress. The work of extending these reactions to other types of enamines has been started.

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4 Spectral data for **2**: TOF-SIMS: m/z 720(C_{60}^+), 804 (M$^+$), 911 (M$^+$+Ag); FT-IR: ν(KBr)/cm^{-1} 2959, 2924, 2882, 1740(s), 1647, 1559, 1540, 1456, 1428, 1400, 1346, 1215, 1184, 1153, 875, 806, 765, 743, 706, 575, 565, 553, 528(s), 512, 475, 419; UV-Vis: (CH_2Cl_2) λmax/nm 229, 254, 306, 430; ^{1}H NMR: (600 MHz, CS_2/CD_3COCD_3 10/1, assigned by HMQC and ^{1}H-^{1}H COSY) δ 6.71 (s, 1H, H-1), 4.27 (m, 1H, H-3'), 3.24-3.21 (m, 2H, H-2'), 3.12 (m, 1H, H-4'), 2.99 (m, 1H, H-4'), 2.70-2.63 (m, 2H, H-5'); ^{13}C NMR: (150.9 MHz, CS_2/CD_3COCD_3 10/1, assigned by ^{1}H-^{1}H COSY, HMQC and HMBC) δ 212.41(C=O), 154.10, 154.01, 153.97, 153.94, 147.95, 147.76, 147,46, 147.44, 147.10, 147.06, 146.90, 146.75, 146.68, 146.27, 146.10, 145.93, 145.90, 145.20, 144.99, 143.76, 143.14, 142.72, 142.70, 142.59, 142.54, 142.30, 142.24, 142.19, 142.14, 142.12, 140.88, 140.46, 137.08, 136.80, 67.91(C-1), 59.13(C-2), 51.86(C-3'), 42.06(C-2'), 39.35(C-5'), 27.50(C-4').

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6 The reaction of **1b** with [60]fullerene was traced by ESR experiment during the first two hours. A weak signal (signal-noise ratio: 2/1) was observed throughout the experiment, which we attributed to the presence of active radical intermediates of low concentration in the reaction.

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9 Spectral data for **8**: FD-MS: m/z 721(C_{60}^++1), 817(M$^+$+1); FT-IR: ν(KBr)/cm^{-1} 2943, 2918, 2852, 1756(s), 1462, 1428, 1281, 1187, 1075, 896, 778, 765, 575, 562, 528(s), 493; UV-Vis: (CH_2Cl_2) λmax/nm 228, 255, 312, 365, 433; ^{1}H NMR: (600 MHz, CS_2/CD_3COCD_3 4/1, assigned by HMQC and ^{1}H-^{1}H COSY) δ 4.08(t, 2H, H-2'), 3.92(m, 1H, H-4), 3.23(m, 2H, H-3'), 2.98(m, 2H, H-3'), 2.20(m, 1H, H-4'); ^{13}C NMR: (150.9 MHz, CS_2/CD_3COCD_3 4/1, assigned by ^{1}H-^{1}H COSY, HMQC and HMBC) δ 213.59(C=O), 156.42, 151.93, 147.78, 147.63, 146.62, 146.55, 146.48, 145.99, 145.93, 145.84, 145.57, 144.96, 143.46, 142.99, 142.43, 142.40, 142.33, 142.29, 142.18, 141.32, 140.82, 140.40, 139.28, 134.56, 67.85(C-1), 57.53(C-2'), 37.46(C-3'), 16.90(C-4').