Pergamon

Tetrahedron Letters, Vol. 36, No. 30, pp. 5383-5384, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)01028-9

Palladium-Catalyzed [3+2] Cycloaddition of 60-Fullerene with *cis*-$HOCH_2CH{=}CHCH_2OCO_2Et$

Clifton K. F. Shen, Kuo-Ming Chien, Tsang-Yu Liu, Tsung-I Lin, Guor-Rong Her, and Tien-Yau Luh*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

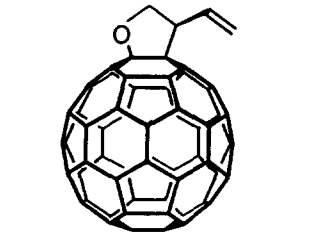
Abstract Palladium-catalyzed [3+2] cycloaddition reaction between 60-fullerene and *cis*-$HOCH_2CH{=}CHCH_2OCO_2Et$ yields the corresponding adduct having 3-vinyltetrahydrofuran skeleton.

Palladium-catalyzed [3+2] cycloaddition reaction has been shown particularly useful in the construction of five-membered ring skeletons.[1] In general, such cycloaddition requires the alkene moiety being electron deficient. The application of this reaction to derivatize 60-fullerene has been rare; only 60-fullerene-TMM adduct was prepared by this method.[2] Since 60-fullerene can be considered as an electron deficient species and various kinds of hard nucleophiles have been shown to add onto the double bond of this polyunsaturated ball,[3] we felt that using the appropriate reactant(s), [3+2] cycloaddition reaction can be achieved leading to the formation of a tetrahydrofuran derivative of 60-fullerene. Herein we report a novel palladium-catalyzed [3+2] cycloaddition of 60-fullerene with *cis*-$HOCH_2CH{=}CHCH_2OCO_2Et$ **2**.

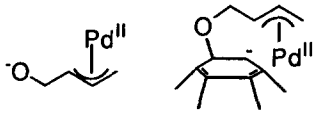
A benzene solution of 60-fullerene was allowed to react at room temperature for 20 h with 1 to 1.5 equivalents of **2** in the presence of 10-50 mol% of $Pd(PPh_3)_4$ and one equivalent of $Ph_2PCH_2CH_2PPh_2$. After usual workup and chromatographic separation on silica gel using hexane-toluene (1:1) as eluent, adduct **1** was obtained in 59% yield.[4] The parent peak at m/z 790 for **1** was observed by electronspray mass spectrometry in the negative ion mode (ESI-MS).[5] The ^1H NMR exhibited absorptions at δ 4.60 (dt, J = 6.2, 9.3 Hz, 1H), 4.83 (t, J = 9.3 Hz,1H), 4.97 (dd, J = 6.2, 9.3 Hz, 1H), 5.51 (dd, J = 1.4, 9.8 Hz, 1H), 5.66 (dt, J =1.4, 16.6 Hz, 1H), and 6.42 (ddd J = 9.3, 9.8, 16.6 Hz, 1H). These data are consistent with the proposed structure having 3-vinyltetrahydrofuran skeleton. Not all ^{13}C NMR absorptions for the 60-fullerene skeletons could be observed due to some overlap among signals. However, the ^{13}C NMR signals for the addend appeared at δ 59.53, 69.95, 119.98, 133.74, and the two sp^3-carbons due to the 60-fullerene fragment exhibited at δ 72.38, 98.88 which agree well with the 3-vinyltetrahydrofuran skeleton. Like many other reactions of 60-fullerene, the cycloaddition with **2** should occur at the two six-membered-ring junction.[6]

The UV-vis spectrum of **1** is shown in Figure 1. The spectrum for 60-fullerene is also included for comparison. It is interesting to note that **1** exhibited the fluorescence emission spectrum with λ_{max} at 702 nm (excitation frequency: 328 nm) which is similar to those of other fullerene derivatives.[7]

Although the mechanism of this reaction has not been established, nucleophilic addition of the π-



1



3 4

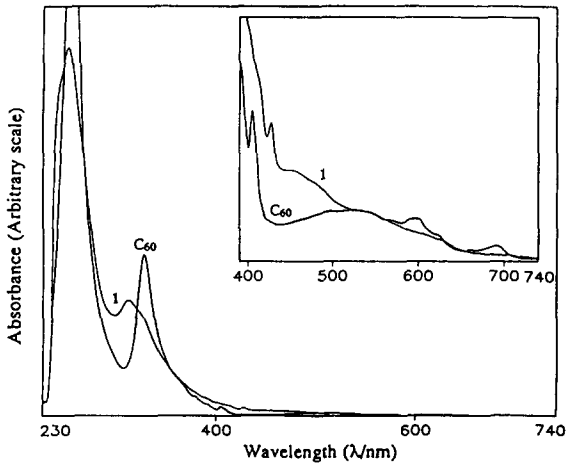


Figure 1 The UV-vis spectra of **1** and 60-fullerene in $CHCl_3$ (1.0 x 10-5 M; 5.0 x 10-5 M in the inset)

allylpalladium alkoxide **3** to 60-fullerene may occur leading to the anion **4** which may undergo another nucleophilic addition to the π-allylpalladium system to give **1**. Surprisingly, attempts to carry out a similar reaction with electron deficient alkenes (such as TCNE) resulted in the isolation of 1-butene-3,4-diol. No cyclization product similar to **1** has been detected at all. The palladium-catalyzed addition of oxygen nucleophile to an electron deficient double bond appears to be difficult;[8] the isolation of **1** might demonstrate typical intrinsic property of 60-fullerene.

Acknowledgment. This work is supported by the National Science Council of the Republic of China.

References and Notes

1. Chan, D. M. T. in *Comprehensive Organic Synthesis* ; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991, Vol. 5, Chap. 3.2.
2. (a) Shiu, L.-L.; Lin, T.-I.; Peng, S.-M.; Her, G.-R.; Ju, D. D.; Lin, S.-K.; Hwang, J.-H.; Mou, C.-Y.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 647. (b) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.
3. (a) Wilson, S. R.; Wu, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10334. (b) Kampe, K. D.; Egger, N.; Vogel, M. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1174.
4. The purity of **1** (>99.3%) has been checked by HPLC using buckyclutcher column. Spectroscopic data for **1**: ^{13}C NMR ($CS_2/CDCl_3$, 100 MHz): δ 59.53, 69.95, 72.38, 98.88, 119.98, 133.74, 135.64, 137.12, 137.36, 137.56, 139.33, 139.45, 139.56, 139.94, 141.26, 141.45, 141.51, 141.81, 141.86, 141.89, 141.94, 141.98, 142.03, 142.05, 142.34, 142.41, 142.45, 142.59, 142.66, 144.12, 144.28, 144.30, 144.41, 144.76, 144.91, 144.94, 145.01, 145.10, 145.16, 145.30, 145.66, 145.76, 145.78, 145.83, 145.98, 146.07, 146.14, 147.10, 147.70, 148.52, 149.73, 151.53, 154.63. IR (KBr) ν 1509, 1461, 1423, 1262, 1172, 1151, 1133, 1106, 1085, 1027, 984, 966, 951, 921, 889, 877, 860, 837, 804, 768, 748, 738, 719, 698, 686, 665 cm^{-1}.
5. Liu, T.-Y.; Shiu, L.-L.; Luh, T.-Y.; Her, G.-R. *Rapid Commun. Mass. Spect.* **1995**, *9*, 93.
6. Shiu, L.-L.; Chien, K.-M.; Tseng, T.-Y.; Lin, T.-I; Her, G.-R.; Luh, T.-Y. *J. Chem. Soc., Perkin 1* **1994**, 3355 and references therein.
7. Lin, S.-K.; Shiu, L.-L.; Chien, K.-M.; Luh, T.-Y.; Lin, T.-I *J. Phys. Chem.* **1995**, *99*, 105.
8. For example, Ohe, K.; Matsuda, H.; Ishihara, T.; Ogoshi, S.; Chatani, N.; Murai, S. *J. Org. Chem.* **1993**, *58*, 1173.

(*Received in China* 6 *March* 1995; *accepted* 5 *May* 1995)