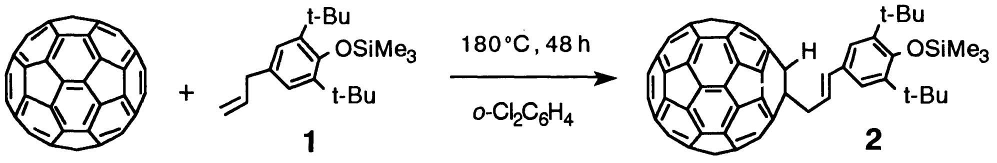
CHEMISTRY LETTERS, pp. 635-636, 1994.

Ene Reaction as a New Method for Functionalization of Fullerene C_{60}

Koichi KOMATSU,* Yasujiro MURATA, Nobuyuki SUGITA, and Terence S. M. WAN †
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611
† Department of Chemistry, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Fullerene C_{60} undergoes the ene reaction when heated with 3,5-di-*t*-butyl-4-(trimethylsiloxy)allylbenzene at 180 °C for 48 h to give the monoadduct in 20% yield.

Study on fullerene C_{60} is now rapidly expanding into the field of organic chemistry.[1)] Among the organic reactions so far reported for C_{60}, probably the best studied would be the [4+2] cycloaddition with the use of one of the π-bonds in C_{60} as a dienophile.[2,3)] However, there has been surprisingly no report on the electronically related ene reaction in spite of its potential applicability.[4)] Here we report a new example of the ene reaction of C_{60} (equation 1). We chose a *p*-allylphenol derivative **1** as an ene moiety from the viewpoint that 1) an electron donating group raises HOMO of the ene molecule thus increasing its reactivity and 2) the hindered phenol moiety in the product has the possibility for conversion into rather stable radical, anion, or quinoid type species so that the electronic interaction between the C_{60} nucleus could be studied.



(1)

The reaction was carried out by heating a solution of C_{60} (35.6 mg, 0.0494 mmol) and the silylated phenol **1** (113 mg, 0.355 mmol) in *o*-dichlorobenzene (3 ml) under argon at 180 °C for 48 h. Separation of the mixture by the use of medium-pressure liquid chromatography (hexane-benzene / silica gel) afforded unchanged C_{60} (8.1 mg, 23%), a dark brown solid assigned as the monoadduct **2** (vide infra) (10.2 mg, 20%), and another solid which was supposed as the bisadduct (4.5 mg, 7%) based on the FAB MS data: *m/z* 1356 ($C_{100}H_{68}O_2Si_2$, M). Either prolonged heating or change in the molar ratio of reagents did not improve the yield. Also no clean reaction was observed when the unprotected allylphenol was used instead of **1**.

The ^1H NMR spectrum (300 MHz, CS_2-$CDCl_3$) of the monoadduct indicated the presence of only one isomer: δ 7.46 (s, 2 H, Ar-H), 7.15 (d, *J*=15.6 Hz, 1 H, =CH-), 6.94 (dt, *J*= 15.6, 7.3 Hz, 1 H, =CH-), 6.60 (s, 1 H, fullerenyl-H), 4.30 (d, *J*=7.3 Hz, 2 H, CH_2), 1.45 (s, 18 H, $C(CH_3)_3$), 0.44 (s, 9 H, $Si(CH_3)_3$). The (*E*)-geometry of the propenyl group is apparent from the value of coupling constant. From the ^{13}C NMR (75 MHz, CS_2-$CDCl_3$) spectrum, which exhibited 32 signals (one signal at δ 145.30 was apparently enhanced by overlapping) for fully substituted sp^2-carbons in the aryl and C_{60} moieties, the ene reaction is considered to have taken place across the 6,6-junction π-bond to give the adduct with the structure **2**: δ 155.62 (s), 153.90 (s), 153.33 (s), 147.34 (s), 147.19 (s), 146.98 (s), 146.30 (s), 146.27 (s), 146.17 (s), 146.14 (s), 146.09 (s), 145.74 (s), 145.43 (s), 145.35 (s), 145.30 (s), 144.62 (s), 144.51 (s), 143.16 (s), 142.97 (s), 142.48 (s), 142.20 (s), 141.96 (s), 141.93 (s), 141.89 (s), 141.58 (s), 141.54 (s), 140.81 (s), 140.23 (s), 140.13 (s), 137.21 (d, =CH-), 136.26 (s), 136.00 (s), 128.99 (s), 124.49 (d, =CH- (aryl)), 121.65 (d, =CH-), 65.02 (s, quaternary C in C_{60} core), 58.72 (d, CH in C_{60} core), 50.63 (t, CH_2), 34.96 (s, $\mathit{C}(CH_3)_3$), 31.16 (q, $C(\mathit{C}H_3)_3$), 3.92 (q, Si-CH_3).

The UV-Vis absorptions were typical for the 1:1 adduct at the 6,6-bond: λ_{max} (C_6H_{12}) 213 nm (log ε 5.15), 257 (5.06), 313 (4.62), 405 (3.68), 433 (3.58), 476 (sh, 3.22), 537 (sh, 3.00), 587 (sh, 2.78), 611 (sh, 2.70), 639 (2.63), 672 (2.42), 694 (2.55), 706 (2.67). The IR absorptions (KBr) were as follows: ν 2954, 1461, 1423, 1391, 1361, 1255, 1232, 1121, 963, 917, 891, 763, 577, 528 cm^{-1}. The molecular formula was confirmed by FAB MS, *m/z* 1039 ($C_{80}H_{35}OSi$, M+H) with an intense peak at 720 (C_{60}), by NH_3 DCI MS, and by analysis. Found: C, 92.19; H, 3.14%. Calcd for $C_{80}H_{34}OSi$: C, 92.46; H, 3.30%.

Thus, the present results indicate that the π-bond shared by two hexagons on the C_{60} surface can act not only as dienophile but also as an enophile. The reaction is considered to take the pathway typical for concerted ene reaction since the reaction was found to be much slower with allylbenzene having no activating substituent.

The cyclic voltammetry5) on the monoadduct **2** exhibited an irreversible oxidation peak at E_{pa} +1.32 V and three reversible reduction waves at $E_{1/2}$ -1.06, -1.48, and -2.04 V vs. ferrocene/ferrocenium. These values coincide with those for C_{60}-anthracene adduct,3,6) and are cathodically shifted by 0.09 - 0.19 V as compared with those for C_{60}.6) This might be considered as due to some intramolecular electronic interaction between the aromatic ring and the C_{60} core, although the effects of inductive electron donation could not be rigorously eliminated.

The present work clearly demonstrated the applicability of the ene reaction for creation of new C_{60} derivatives with novel electronic properties. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 05233220) from the Ministry of Education, Science and Culture, Japan.

References

1) For reviews, see R. Taylor and D. R. M. Walton, *Nature*, **363**, 685 (1993); G. A. Olah, I. Bucsi, R. Aniszfeld, and G. K. S. Prakash, *Carbon*, **30**, 1203 (1992); P. J. Fagan, B. Chase, J. C. Calabrese, D. A. Dixon, R. Harlow, P. J. Krusic, N. Matsuzawa, F. N. Tebbe, D. L. Thorn, and E. Wasserman, *ibid.*, **30**, 1213 (1992).
2) For example, see M. Ohno, T. Azuma, and S. Eguchi, *Chem. Lett.*, **1993**, 1833, and the references cited.
3) K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, and T. S. M. Wan, *Tetrahedron Lett.*, **34**, 8473 (1993).
4) When we finished preparing this manuscript, we learned that an independent study on the ene reaction of C_{60} with *p*-allylanisole is being reported by Professor S-H. Wu of Fudan University: S-H. Wu et al., *Tetrahedron Lett.*, in press. We thank Professor Wu for this information.
5) Measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 M) as a supporting electrolyte (sample concentration, 0.5 mM); scan rate, 0.1 $V{\cdot}s^{-1}$.
6) For comparison of the data taken under the same conditions, see K. Komatsu, A. Kagayama, Y. Murata, N. Sugita, K. Kobayashi, S. Nagase, and T. S. M. Wan, *Chem. Lett.*, **1993**, 2163.

(Received December 20, 1993)