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# ENE REACTION OF FULLERENE $C_{60}$ AND 4-ALLYLANISOLE. INTRODUCTION OF ALKENE TO BUCKMINSTERFULLERENE[1]

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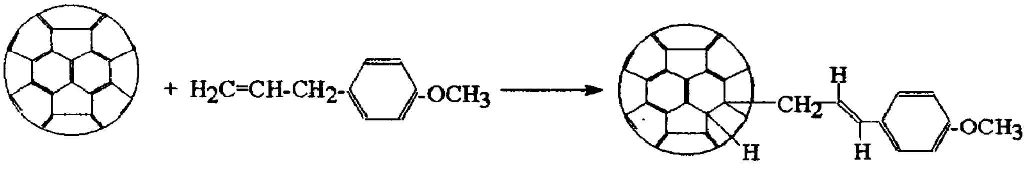
***Abstract:*** *4-Allylanisole reacts with $C_{60}$ at 200~220°C to form ene reaction adducts; The monoadduct was isolated by flash column chromatography and structurally characterized by FAB-MS, UV-VIS, IR, $^1H$-NMR spectroscopies.*

Since the success of preparation and separation of fullerenes on a preparative scale,[2] many chemists have been attracted to study fullerenes' versatile chemical and physical properties.[3] Among the various types of reactions of fullerenes, e.g., electrophilic reactions,[3] reduction[4] and oxidation,[5] the cycloaddition reactions[6] play an important role in the functionalization of fullerenes. The pyracyclene model and knowledge of the high reactivity of the double bond at the junction of two hexagons[3] lead us to study the ene reaction of $C_{60}$ and alkenes for the introduction of an alkene group to the $C_{60}$ molecule.

We tried the ene reaction between 1-heptene and $C_{60}$ first. After heating a mixture of $C_{60}$ and 1-heptene for 10 hours at 200°C, a mixture of adducts was obtained. The fast atom bombardment mass spectrometry(FAB MS)[7] shows that there are three peaks higher than 720, i.e., 818 (monoadduct), 917(diadduct), and 1015(triadduct). But in seeking for an isolation procedure of the pure compounds, neither high-performance thin layer chromatography (HPTLC) nor high-performance liquid chromatography (HPLC) gave a single pure adduct. We designed a new substrate 4-allylanisole(1), which possesses a polar anisole moiety together with the reactive allylic function for the ene reaction.



1 2

The ene reaction adducts of $C_{60}$ and 4-allylanisole (**1**) are obtained after heating for 15 hours at 200~220°C. The isolated yield of **2** is 38% (based on consumed $C_{60}$). It becomes easier to separate $C_{60}$ from the monoadduct(**2**) because of the great difference in polarity. The HPTLC on silica gel gives a spot($R_f$=0.64) for the monoadduct, when n-hexane and methylene chloride (3:1) is used as the eluent. Thus both the HPLC and flash column chromatography can very well separate the unreacted $C_{60}$ from the monoadduct.

FAB mass spectrometry of monoadduct ($C_{70}H_{12}O$) displays a peak at 869 as well as one for $C_{60}$ at 720 which arises from loss of $C_{10}H_{12}O$. The electronic absorption spectra of the monoadduct in hexane showed that it is similar to the spectra of $C_{60}$ in ultraviolet region at wave length less than 300 nm. Two strong absorption bands at 213 and 257 nm are observed. But they are different in the weakly absorbing bands of the ultraviolet and visible region. There is a new weak absorption band at 310 nm, and the absorption band of $C_{60}$ at 330 nm changes to a shoulder. In the visible region two new absorption bands at 431 and 706 nm are observed while the weak absorptions at 540 and 600 nm almost disappear. In Fourier transform infrared (FT-IR) spectrum the main C-C vibration bands of **2** are shifted slightly from those of $C_{60}$(corresponding $C_{60}$ absorbance parenthesized): 1425.0(1429), 1171.9(1181), 562.5(572), 528.1(528.1) $cm^{-1}$. Both a weak unsaturated C-H stretch at 3025.0 $cm^{-1}$ and a middle *trans*-ethylenic hydrogen out of plane bend is observed at 965.6 $cm^{-1}$.The aromatic ring stretch vibration bands are located at 1606.2 and 1509.4 $cm^{-1}$. The stretch vibration band for methyl ether is located at 1246.9 $cm^{-1}$.

In $^1H$ nuclear magnetic resonance ($^1H$-NMR) spectrum[8] the following signals are observed in $CDCl_3$ at $\delta$ 3.87(s, 3H, $OCH_3$), 4.32(d, 2H, $CH_2$, $J$=7.1 Hz), 6.60(s, 1H, $C_{60}$-H), 6.98(d,2H, Ar-H), 7.06(txd,1H, ethylenic-H, $J_t$=7.1 Hz, $J_d$=15.7 Hz), 7.21(d,1H, ethylenic-H, $J$=15.7 Hz), 7.61(d, 2H, Ar-H) ppm. The signal at 6.60 ppm shows that it is the $C_{60}$- H transition, which also indicates 1,2-substituted $C_{60}$-H.[9] The signals at 6.98 and 7.61 ppm are a part of pattern of AA'XX' splitting for the four aromatic protons of the monoadduct (**2**) of the ene reaction . Both the coupling constant $J$ =15.7 Hz for ethylenic proton in $^1H$-NMR spectrum and the middle intensity absorbing band at 965.6 $cm^{-1}$ in FT-IR show that there is a *trans*-ethylenic link in the adduct molecule. This feature is consistent with the characteristic chair conformation of the transition state of ene reaction. These spectroscopical data are fully consistent with expectations for the structure of **2**. The experimental finding for **2** was confirmed by semiempirical molecular orbital calculations with MNDO program on the reaction of $C_{60}$ and 4-allylanisole. Both 1-(4-methoxyphenyl)allyl and hydrogen atom are added at the junction of two six-membered rings in $C_{60}$ to give a 6-6 adduct **2a** which is 25.9 Kcal/mol more stable than the isomeric **2b**(a 5-6 adduct). Interestingly, this is mostly consistent with the addition of diphenylsilylene, for which the 6-6 adduct was calculated to be 19.4 Kcal/mol more stable than the 5-6 adduct[6g].

The isolated monoadduct of this ene reaction is a dark brown microcrystalline powder. Structure analysis by X-ray diffraction is in progress.

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