

Chemical Transformation of Fullerene C₆₀

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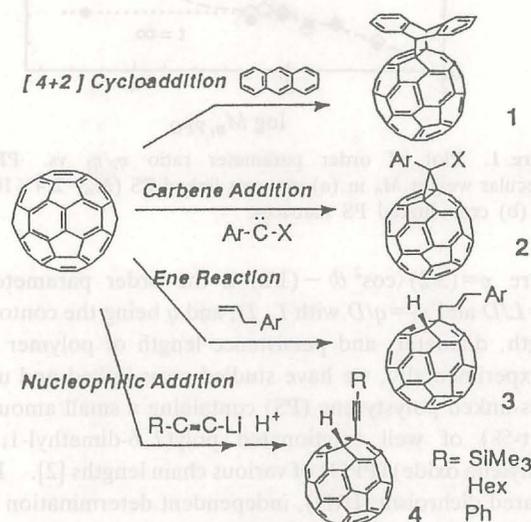
The fullerene C₆₀ reacts with dienes, carbenes, allylbenzenes, and lithium acetylides, at one of the juncture bonds between six-membered rings on the π -surface to give 1:1 adducts. Cyclic voltammetry on these adducts indicate that the intrinsic electronic properties of original C₆₀ are essentially maintained in these adducts. The first acetylene derivative of C₆₀ thus prepared gives a stable fullereryl carbanion, which is fully characterized by ¹H and ¹³C NMR as well as by CV. Reactions of this carbanion with various electrophiles give new difunctional derivatives.

Keywords: Carbon cluster/ [4+2] addition/ Carbene addition/ Acetylenic C₆₀/ CV/ Redox behavior

Since the successful preparation of fullerene C₆₀ in macroscopic amount by Krätschmer and Huffman in 1990, the chemistry on C₆₀ has met with explosive development. The chemical transformation of C₆₀ is not only intriguing from a purely academic viewpoint but requisite for exploiting the applicability of this totally new carbon allotrope as a functional material.

We have investigated transformation of C₆₀ as summarized in Scheme 1, in order to examine the possible intramolecular electronic interaction of an electronegative core of C₆₀ with rigidly held π -systems (compound 1) [1], to introduce a supposedly reactive benzylic C-X bond (compound 2) [2] and olefinic functionalization (compound 3) [3] to C₆₀, and to attach a triple bond to the C₆₀ π -surface (compound 4) [4]. All the reactions have been found to take place specifically at one of the thirty π -bonds at the juncture between six-membered rings of C₆₀ as judged from the results of the ¹³C NMR spectral analysis.

The redox behaviors of all the newly synthesized C₆₀



Scheme 1

ORGANIC MATERIALS CHEMISTRY —High-Pressure Organic Chemistry—

Scope of research

Fundamental studies are being made for utilization of high pressure in organic synthesis and for creation of new functional materials with novel structures and properties. The major subjects are: utilization of carbon monoxide and dioxide for organic synthesis; studies on the transition-metal catalyzed photochemical carbonylation; synthetic and structural studies on novel cyclic π -systems; chemical transformation of fullerene C₆₀.



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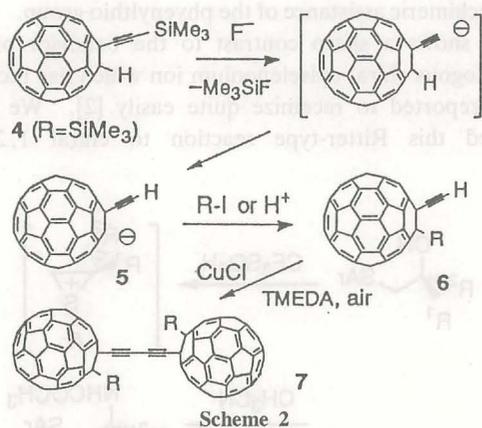
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derivatives were examined by cyclic voltammetry (CV). As shown by the typical voltammogram of **2** (Ar=Ph; X=Cl) in Fig. 1, reversible reduction waves are observed at -1.00 , -1.44 , and -1.97 V vs Ag/Ag⁺ together with an irreversible oxidation peak at $+1.39$ V, which are essentially similar to those of C₆₀ itself. These observations clearly indicate that the original electronic properties of C₆₀ are retained in these derivatives in spite of partial loss of full π -conjugation on the spherical surface of the fullerene molecule.

Compound **4** is the first C₆₀ derivative having a directly attached acetylene functionality. Desilylation of the trimethylsilyl group of **4** (R=Si(CH₃)₃) by fluoride ion was found to be immediately followed by proton migration to afford the fullereryl carbanion **5**, which can be quenched by proton acid or alkyl iodides to give the corresponding difunctional derivatives **6** (Scheme 2). The oxidative coupling of the ethynyl group of **6** gives a new dimer of acetylenic C₆₀, **7**.



Reflecting the high acidity due to the prominent electronegativity of the C₆₀ core, the fullereryl proton of **4** (R=Hex) is readily abstracted by *t*-butoxide in THF to give a dark green solution of the stable fullereryl carbanion **8**, which has a near IR absorption at λ_{max} 990 nm and is fully characterized by ¹H and ¹³C NMR (28 signals between δ 158.42 and 135.01, together with signals at δ 175.24, 120.99, 86.47, 83.40, 54.61, 32.51, 30.22, 29.85, 23.50, 20.50, and 14.44). The CV on this carbanion in THF demonstrates that the oxidation to the corresponding radical occurs at -0.39 V but this process is not reversible due to rapid dimerization of the radical. The reduction peak of this fullereryl dimer, which is associated with dissociation to the monomeric anion, is observed at -1.20 V.

The carbanion **8** reacts with various alkyl and acyl halides to afford the 1,2-bisadducts **9** as shown in Scheme 3

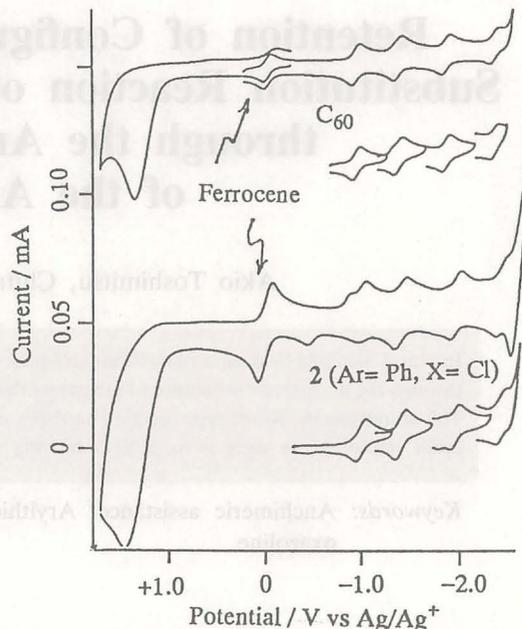
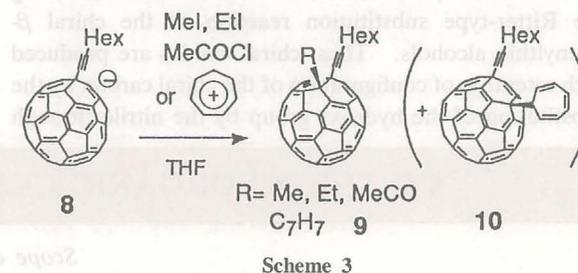


Figure 1. Cyclic voltammograms of C₆₀ and of **2** (Ar=Ph, X=Cl) in benzonitrile; scan rate $0.1 \text{ V} \cdot \text{s}^{-1}$.

3. In contrast, the reaction with the more sterically demanding electrophile such as tropylium ion gives a 1:1 mixture of the 1,2- (**9**) and 1,4-bisadducts (**10**). These results can be successfully interpreted by theoretical calculations using semi-empirical MO methods. A work is now underway to prepare a polymer-bound C₆₀ derivative in collaboration with Professor Miyamoto's group in this institute.



References

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