

### Lecture 3. Functionalized Fullerenes. Applications of Fullerenes

**The purpose of the lecture:** to provide information on the functionalized fullerenes and applications of fullerenes.

**Expected results:** to know the features of the functionalized fullerenes and applications of fullerenes.

The enormous potential of fullerenes in practical materials science and biological applications is limited by hydrophobicity of the carbon cage and limited solubility of fullerenes in polar solvents combined with their aggregation tendency, which further reduces their solubility. These processing difficulties can be overcome by organic derivatization of fullerenes through various reactions to obtain chemically modified fullerenes.

Functionalization can help to convert the hydrophobic surfaces of fullerenes to provide hydrophilic surfaces for diagnostic purposes and therapeutic purposes. These reactions help to develop new fullerene products through introduction of useful extensions to the fullerene sphere. These extensions alter their properties, for instance, solubility and electrochemical behavior, and therefore widen the range of applications in the field of materials science and technology. The basic principles of organic chemistry of fullerenes have been summarized by Prato.

The C<sub>60</sub> has conjugated double bonds but all the double bonds are localized in the hexagon rings. It, therefore, is not a superaromatic compound but rather a polyene. The reactivity of C<sub>60</sub> is that of a strained electron-deficient alkene with high electron affinity. C<sub>60</sub> behaves as an electrophile and reacts readily with electron-rich species or nucleophiles and undergoes nucleophilic addition reactions. Due to the closed cage structure of C<sub>60</sub> the attacking agents can be added only to the exohedral surface of C<sub>60</sub>, and most reactions occur at the highly reactive hexagon-hexagon edges between two pentagon rings. The driving force for these reactions is the relief of steric strain.

Some of the important reactions of C<sub>60</sub> are the Bingel reaction (nucleophilic cyclopropanation of C<sub>60</sub> to a methanofullerene), [4 + 2] cycloaddition or the Diels Alder reaction, [3 + 2] cycloaddition or the Prato reaction and [2 + 2] cycloaddition. Figure 1 shows the important functionalization reactions of C<sub>60</sub>.

Functionalized fullerenes containing 3-, 4-, 5-, and 6-membered rings built onto or across a 6,6 ring junction of C<sub>60</sub> can be obtained by a variety of reactions. The Bingel Hirsch reaction, or the Bingel reaction, is one of the most valuable functionalization reactions of fullerenes. It involves a nucleophilic attack of a bromomalonate on a double bond of a fullerene in the course of which a cyclopropane ring (three-membered ring) is generated to give a methanofullerene with a bridged (6,6) bond. The Diels Alder reaction is another very important reaction of C<sub>60</sub>.

The 6,6 double bonds of C<sub>60</sub> act as dienophiles and undergo [4 + 2] cycloaddition reactions with a variety of dienes (Figure 1d). As shown in Figure 1d, the classical Diels Alder reaction produces a six-membered ring. The Prato reaction is the [3 + 2] cycloaddition reaction that was applied to fullerenes by Prato. This fullerene functionalization reaction is based on the 1,3-dipolar cycloaddition of azomethine ylides to C<sub>60</sub> and is a powerful and widely used methodology (Figure 1c) because of the versatility of the reactions and the stability of the resulting fulleropyrrolidines. A mixture of amino acid and paraformaldehyde are refluxed in toluene to yield an ylide that reacts with the 6,6 double bond in C<sub>60</sub> via 1,3 -dipolar cycloaddition to yield a five-membered ring pyrrolidine derivative called N-methyl pyrrolidine. Azomethine ylides can be obtained from a wide variety of easily accessible starting materials and react readily with C<sub>60</sub>. The substituted pyrrolidine products can be further functionalized. Cyclobutano fullerene derivatives are typically obtained by [2 + 2] cycloaddition reactions as shown in Figure 1b.

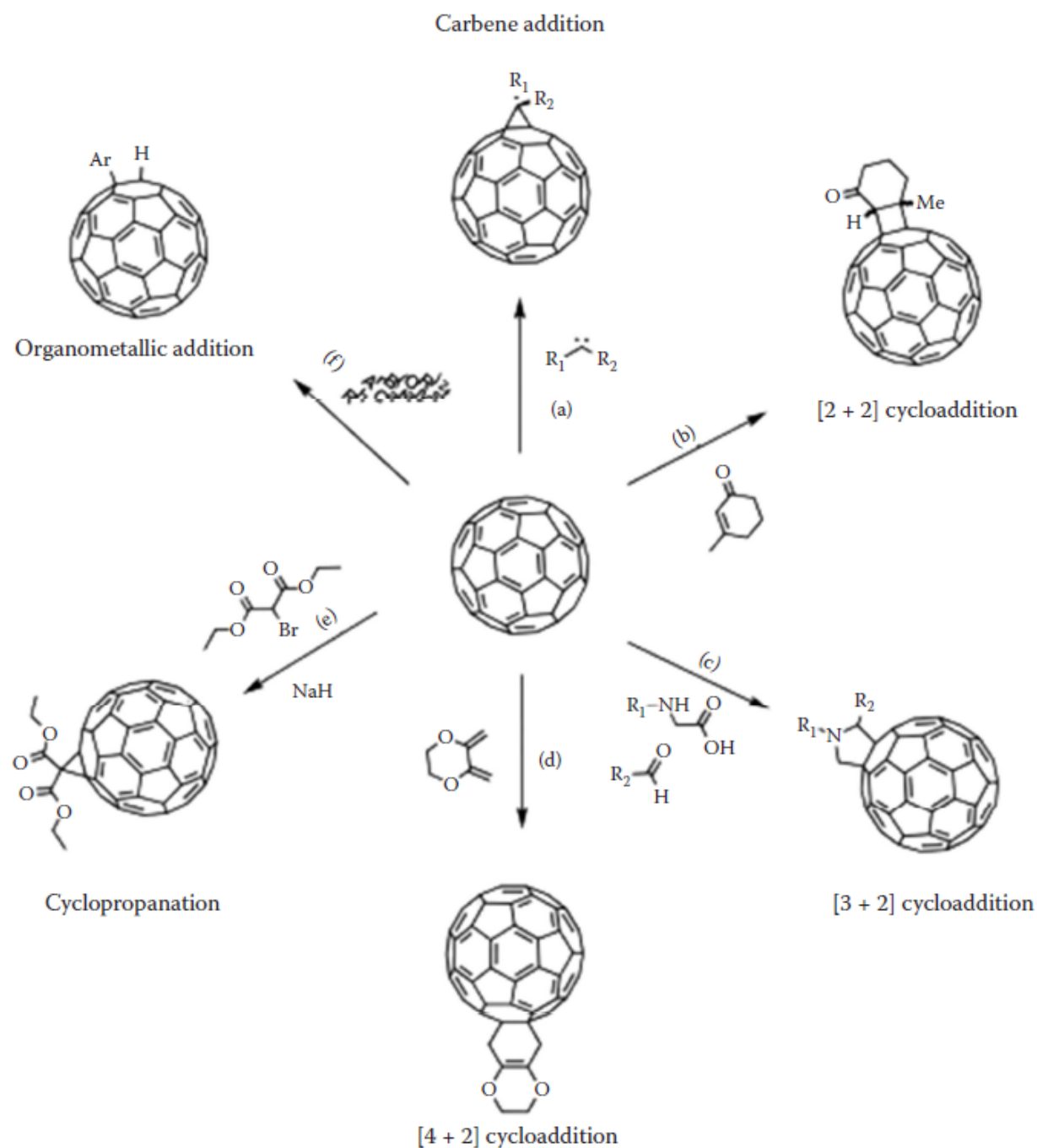


FIGURE 1. Covalent functionalization reactions of C60 (a) [1 + 2] cycloaddition; (b) [2 + 2] thermal cycloaddition; (c) [3 + 2] cycloaddition with azomethine ylides; (d) [4 + 2] Diels–Alder cycloaddition; (e) Bingel–Hirsch reaction; and (f) Rh-catalyzed arylation.