Organic chemistry with buckminsterfullerene ($C_{60}$)

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A brief review of the organic chemical reactions with buckminsterfullerene ($C_{60}$) – Birch reduction, reductive alkylation, halogenation, Friedel-Crafts reaction, dipolar cycloaddition – that have been reported in the literature is presented. Some preliminary results on hydroboration–protonolysis, cycloaddition of diazomethane and chlorosulfonyl isocyanate with $C_{60}$ have been discussed.

Carbon is the all important element that anchors the molecules of everything from crude oil to DNA and is thus a kind of natural backbone. In recent years, a number of groups of scientists have been pursuing an exotic form of carbon believed to have a particularly elegant configuration: 60 atoms of carbons arranged like a miniature soccer ball. In 1990, a team of astronomers led by Kratschmer and Huffman reported that this new allotrope of carbon, $C_{60}$, named buckminsterfullerene, can be produced in reasonable quantities through resistive heating of graphite under inert atmosphere.

They found that the sublimate from the arc-processed graphite was soluble in benzene and contained a range of fullerenes, $C_{60}$ and $C_{70}$ in particular. This material was chromatographed by using hexane/alumina and $C_{60}$ and $C_{70}$ were thereby separated into magenta and red coloured fractions respectively. $^{13}$C NMR measurements of $C_{60}$ showed a single line ($\delta 142.68$) suggesting that all the 60 atoms are equivalent. The $^{13}$C NMR spectrum of $C_{70}$ consisted of a set of five lines indicating five different types of carbons in the ratio 10:10:20:20:10. The structures in Fig. 1 and Fig. 2 for $C_{60}$ and $C_{70}$ are also supported by IR, Raman and photoelectron spectroscopy. The ultimate configuration and the detailed parameters of the soccer ball shaped framework had to wait for X-ray crystallographic analysis. But the crystals of $C_{60}$ were disorganised piles of buckyballs and there was no way of viewing the individual molecules, because $C_{60}$ is the most symmetric molecule possible in three-dimensional Euclidean space; it is the roundest of round molecules; edgeless, chargeless, and unbound. The major difficulty arises from the fact that when the buckyballs are on their own, they spin like tiny planets completing more than billion rotations in a second. They do not stay still long enough to have their picture taken. To break the symmetry of $C_{60}$ and prevent its rapid spinning in the crystal, Hawkins et al. prepared by osmylation a 1:1 $C_{60}$-osmium tetroxide adduct. (Eq. 1).

The crystal structure of this adduct was finally solved which clearly confirms the soccer ball structure of $C_{60}$ consisting of 20 six-membered rings fused to 12 five-membered rings. All tricordinate carbon atoms of $C_{60}$ are pyramidalized...
and lie at an average distance of 3.5 Å from the center of the sphere. The bond length at the six-six ring fusion is 1.39 Å and the bond length at the five-six ring fusion is 1.43 Å. The UV/vis spectrum showed absorption at 213, 257, 329 (λmax 500, 540, 570, 600, 625) nm and infrared spectrum had absorptions at 528, 579, 1183 and 1429 cm⁻¹ (refs 1,5).

The name chosen for the molecule buckminsterfullerene is long but definitely not as long as the IUPAC nomenclature (Fig. 3)⁷. The name 'fullerene' is conveniently used for the whole family of closed carbon cages with the 12 pentagons and N (other than one) hexagons in an sp² network⁴⁹,¹¹.

Organic chemical reactivity of fullerene-60

Since improved and simple experimental set up and techniques for the production of fullerenes in significant quantities are available now¹²⁻¹⁴, a new era of polycyclic aromatic chemistry has started. C₆₀, however, differs in many respects from the planar aromatic molecules and exhibits "ambiguous" aromatic character¹⁵. The structural framework in C₆₀ is generally very stable and it possesses a relatively small π-electron ring current magnetic susceptibility compared to graphite or benzene¹⁶. Based on electrochemical studies, C₆₀ has been found to be as strong an oxidizing agent as methyl viologen and flavin chromophores and its first reduction potential is more positive than that for most of the polycyclic aromatic hydrocarbons¹⁷. A few organic chemical reactions that have been successfully carried out with C₆₀ so far owe their origin to the inherent electron deficient nature of the molecule.

Reduction and reductive alkylation on C₆₀

Smalley et al.¹² were the first to effect an organic chemical reaction on C₆₀. In a remarkably successful experiment underscoring the aromatic character of fullerene-60, Birch reduction was performed with lithium and liquid ammonia in the presence of t-butanol as proton source to obtain a light cream to off white solid. This material was homogeneous on thin layer chromatographic analysis (Rₜ = 0.37, 30% CH₂Cl₂ in hexanes). However, mass spectral analysis showed this to be a mixture of two hydrocarbons. The major product with the molecular ion at m/z 756 corresponds to the hydrocarbon of formula C₆₀H₃₆. It was not clear whether the minor product with molecular ion at m/z 738 (C₆₀H₃₈) was a genuine coproduct in Birch reduction or the pyrolysis product of C₆₀H₃₆. Based on ¹H NMR spectrum of C₆₀H₃₆ (broad multiplet between δ 2.5 and 4.2) and its analogy with the spectrum of dodecahedrane, the structure of one possible isomer of C₆₀H₃₆ has been postulated as in Fig. 4. Smalley et al. have a convincing explanation for the observation that 36 hydrogens have been added to C₆₀ on Birch reduction. Since Birch reduction affects only conjugated double bonds, 36 is the number of hydrogens required to leave 12 double bonds which are isolated from each other, one on each pentagon (Fig. 4)¹⁸.

The IR spectrum (KBr) of this material exhibited bands at 2925, 2855; 1620, 1450, 1400 and 675 cm⁻¹ strongly supporting the structure with C−H and C=C bonds. To substantiate the point that in the Birch reduction of C₆₀ the basic molecular skeleton of the fullerene has not been al-
tered, Smalley et al. elegantly demonstrated that the reduction is fully reversible. Thus, dehydrogenation of the hydrocarbon C_{60}H_{36} with DDQ in toluene under reflux resulted in the formation of C_{60}^{12+}.

Olah et al. reduced a mixture of C_{60} and C_{70} (approximately 85:15 ratio) using lithium metal in deuterated THF with the aid of ultrasound. Although the fullerenes are only slightly soluble in THF, the reduced fullerenes are highly soluble and generate a deep reddish brown solution of diamagnetic polyanions. The $^{13}$C NMR spectrum at room temperature showed a single resonance at 156.7 ppm for the reduced C_{60}. This deshielding of 14 ppm is a remarkable observation since carbon-carbon carbons are generally shielded compared to their neutral precursors. The reduced C_{70} also showed a similar deshielding effect in the $^{13}$C NMR compared to C_{70}. Subsequent alkylations of these anions with excess methyl iodide yielded a light brown solid. Based on field ionisation mass spectral analysis Olah concluded that it is a mixture of polymethylated fullerenes: all the way up to 24 methyl groups are covalently added to the sphere. This report is the first successful attempt at functionalization of C_{60} and C_{70} via alkylative carbon-carbon bond formation. Obviously this opens up the possibility of functionalization with other alkyl halides and other substituents like trialkylhalosilanes.

Olah et al. also carried out oxidation studies on C_{60} and C_{70} using SbF_{5} in SO_{2}ClIF solution, a system which has been shown to be efficient for the oxidation of polycyclic aromatics to their dications. Green coloured solution thus obtained showed broad $^{13}$C NMR spectra at all temperatures studied. It is very likely that radical cations are generated and no diamagnetic di or polycations are formed.

### Halogenation studies with fullerene-60

There has been some speculation as to the possible lubricant properties of the fully fluorinated fullerene. Initially when fluorination was carried out with XeF_{2}, a mixture of partially fluorinated fullerenes was obtained containing mostly of C_{60}F_{5} and C_{60}F_{12}. Holloway et al. carried out fluorinations on C_{60} with fluorine gas (3-4 days) which reacts slowly in a stepwise manner to obtain finally an almost colourless crystalline product (m.p. 287°C). This compound showed sharp singlet at 153.9 in $^{19}$F NMR spectrum suggesting the environment of fluorine is similar to that expected for C_{60}F_{5}. The IR spectrum had strong absorptions at 1060 and 1035 cm$^{-1}$ indicating the presence of C–F stretching band. The results have been interpreted suggesting fluorination is initially slow owing to the high stability of the fullerene cage. But once the first fluorine molecule has been added the other two bonds in a given benzenoid ring gets fluorinated more rapidly to give C_{60}F_{5}. It is then possible to get a second derivative of enhanced stability, possibly C_{60}F_{12}.

Recently Olah reported studies on chlorination and bromination of fullerenes. Although chlorination was found to be sluggish at room temperature, in a hot glass tube under a slow stream of chlorine gas at 200°C for 5 h, chlorination took place readily to yield a dark brown product containing on an average 24 chlorine atoms (Eq. 2).

$$C_{60} + Cl_{2} \rightarrow C_{60}Cl_{n}$$ ... (2)

Efforts to obtain the mass spectrum of this compound were not successful. The polychloro-fullerene mixture on treatment with excess methanol/KOH under reflux provided a polymethoxylated product (polymethoxylation upto 26 methoxy groups, M$^+$, 1256) (Eq. 3).

$$C_{60}Cl_{n} \xrightarrow{OH-KOH, reflux} C_{60}(OME)_{n}$$ ... (3)

The replacement of methoxy groups has been rationalized by a unique front side substitution.

Interestingly Olah et al. have also shown that the polychlorinated fullerenes undergo Friedel-Crafts reaction (Eq. 4).

$$C_{60}Cl_{n} \xrightarrow{AlCl_{3}, reflux} C_{60}(Ph)_{n}$$ ... (4)

The brown solid obtained on Friedel-Crafts reaction with benzene showed a broad absorption at $\delta$ 7.2 in the $^{1}$H NMR spectrum and a broad absorption at $\delta$ 128 was observed in the $^{13}$C NMR spectrum. Analysis of the FAB mass spectrum revealed substitution of 22 phenyl groups in the molecule.

It was also demonstrated by these authors that bromination of fullerene-60 however takes place at lower temperature (20-50°C) to afford a product with an uptake of two to four bromine atoms (Eq. 5).

$$C_{60} \xrightarrow{Br_{2} (neat)} C_{60}Br_{n}$$ ... (5)

n = 2 or 4

The halogenated fullerenes have been found to undergo thermal dehalogenation to give back fullerenes.

Independently Rao et al. have carried out the
reaction of $C_{60}$ with excess SbCl$_5$ in CCl$_4$ solution to obtain the chlorine adduct as a brown solid which showed C–Cl stretching bands around 812 cm$^{-1}$ in the IR and UV absorption maxima at 250 nm. They have also shown that liquid bromine reacts with $C_{60}$ to give an orange colored product containing the dibromo adduct (C–Br stretching, 515-575 cm$^{-1}$; UV 282 and 330 nm). Attempted reaction of $C_{60}$ with I$_2$ vapor in a sealed tube around 250°C failed to yield any product$^{21}$.

**Acid catalysed fulleration of aromatics**

In a related development on the functionalization of fullerenes, Olah et al.$^{23}$ observed that $C_{60}$ as well as $C_{60}/C_{70}$ mixture undergo Friedel-Crafts reaction with aromatics such as benzene and toluene under catalysis with AlCl$_3$ or strong acids to form polyarenefullerenes (Eq-6).

$$C_{60} \text{H-Ar (excess)} \xrightarrow{AlCl_3} C_{60}(H\text{-Ar})_n \quad \ldots \quad (6)$$

In the reaction with benzene at room temperature after 2 h fullerenes gave a major product identified as $C_{60}(\text{Ph})_{12}$ ($M^+$, 1656). There were other products corresponding to various species containing various amount of benzene adducts. Similarly Friedel-Crafts reaction product with toluene has been identified as $C_{60}(\text{PhCH}_3)_{12}$. A mechanism that has been proposed to explain the formation of the polyarenefullerenes (Scheme-1)$^{23}$ is similar to the alkylation with alkenes under acid catalysis.

**Systematic inflation of fullerene $C_{60}$ with diphenylidazomethane: Synthesis of fulleroids**

Recently Wudl et al.$^{24}$ have demonstrated the dipolarophilicity of $C_{60}$ by reacting it with diphenylidazomethane at room temperature (1 h) to obtain a monoadduct diphenyl fulleroid $C_{61}$ (Fig. 5). Since the electronic spectrum of this compound was strikingly similar to the spectrum of $C_{60}$, the structure in Fig. 5 has been favoured over structure depicted in Fig. 6 for the product. The mechanism of formation of this product has been rationalized by these authors as depicted in Scheme-2 which involves a crucial norcaradiene-cycloheptatriene rearrangement. It has also been found that more extended reaction times with different stoichiometries afforded the diphenyl fulleroids $C_{62}$, $C_{63}$, $C_{64}$, $C_{65}$ and $C_{66}$. These results clearly indicate that one could prepare essentially any functionalized fulleroid.

**Nucleophilic addition to $C_{60}$**

The electron deficient character of $C_{60}$ has
been further confirmed by effecting nucleophilic additions to \( \text{C}_{60} \). Wudl et al. observed multiple additions of amine nucleophiles to \( \text{C}_{60} \) and were able to prepare polyaminated derivatives that are soluble in water.

Rao et al. have carried out detailed studies of addition of aliphatic amines to \( \text{C}_{60} \) and \( \text{C}_{70} \). They have obtained an essentially 1:1 amine adduct by refluxing \( \text{C}_{60} \) with \( n \)-butylamine in toluene (Eq. 7).

\[
\text{C}_{60} + n\text{C}_4\text{H}_9\text{NH}_2 \xrightarrow{\text{Toluene}} n\text{C}_4\text{H}_9\text{NHC}_6\text{H}_{10} \]

\( \cdots \) (7)

Reaction of \( \text{C}_{60} \) with excess methylamine, however has been shown to give a mixture of adducts. Mass spectral analysis revealed this mixture to contain predominantly addition products arising out of 1, 2 and 6 amine units.

**Hydroboration and protonolysis of \( \text{C}_{60} \)**

Since it has earlier been shown that \( \text{C}_{60} \) is rather easily reduced and undergoes nucleophilic addition reactions, not many successful electrophilic addition reactions have been reported. Study of electrophilic addition of borane (BH\(_3\)) to \( \text{C}_{60} \) appeared quite attractive. Accordingly when \( \text{C}_{60} \) in toluene was treated with an excess of BH\(_3\)S(Me)\(_2\) at room temperature (12 h) it resulted in the complete disappearance of the magenta colour of \( \text{C}_{60} \) and a pale brown solid was obtained as the product. The compound showed a broad singlet (\( \delta \) 23.0) in the \( ^1\text{H} \) NMR and the IR spectrum revealed the presence of B−H and C−H stretching bands. Efforts to obtain mass spectrum (electron impact) were not successful. However, protonolysis of the organoborane with propionic acid (reflux, 12 h) afforded a hydrocarbon mixture. Mass spectral analysis revealed the presence of two major products \( \text{C}_{60}\text{H}_{42} \) (M\(^+\) 762) and \( \text{C}_{60}\text{H}_{20} \) (M\(^+\) 740). Efforts are being continued to optimise the reaction conditions and characterize the products fully. It appears as though this methodology can be extended further to obtain the elusive, fully saturated, buckminsterfullerene-\( \text{C}_{60}\text{H}_{60} \).

**Dipolar cycloaddition with \( \text{C}_{60} \)**

In an independent study, we have carried out a \( 1,3 \)-dipolar cycloaddition reaction of \( \text{C}_{60} \) with diazomethane. Reaction of \( \text{C}_{60} \) in toluene and diazomethane in ether takes place readily at room temperature to produce a light brown solid. The product shows C−H stretching bands in the IR spectrum and the UV spectrum has strong absorptions at 272, 312 and 334 nm (cyclohexane).

Although the compound needs to be fully characterized, from mass spectral analysis it appears as though 10 diazomethane units have been added and that the pyrazoline derivative readily eliminates 10 molecules of nitrogen to give a cyclopropyl derivative-\( \text{C}_{60}(\text{CH}_2)_{10} \).

Since \( \text{C}_{60} \) readily undergoes dipolar cycloaddition a study of the reaction of a number of dipolarophiles like phenylazide, nitrones and nitrile oxides would be of much interest. It would thus be possible to make a variety of heterocycles based on \( \text{C}_{60} \).

**(2+2) Cycloaddition with chlorosulfonyl isocyanate**

Although it has been reported that \( \text{C}_{60} \) does not undergo \( 4+2 \) cycloaddition in Diels-Alder fashion, it seems possible to effect \( 2+2 \) cycloaddition with \( \text{C}_{60} \). In an exploratory reaction chlorosulfonyl isocyanate was allowed to react with \( \text{C}_{60} \) in toluene at room temperature. No reaction occurred under these conditions. However when the reaction mixture was heated to 80-100°C, the colour of the solution of \( \text{C}_{60} \) disappeared completely within two hours to produce a mixture of products. Work is under progress to purify and characterize the components. We believe that this methodology would lead to a \( 1,2 \)-functionalized \( \text{C}_{60} \)−\( \beta \)-amino acid with a \( \text{C}_{60} \) skeleton.

Already fullerene chemistry is a vibrant field of study and the prospects for new materials with novel properties is most promising. There will be rich organic chemistry associated with the ‘outside’ of the molecule in the years to come.

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**References**