Chemistry

The Synthesis and Characterization of 2,4,6-Cycloheptatriene-\(C_{60}\) [6,6] Closed Methanofullerene

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\(C_{60}\), also called Fullerene, 1, is a spherical molecule with 60 carbon atoms that looks like a soccer ball (Figure 1). The molecule contains fused five and six membered carbon rings. The addition of one carbon atom to the \(C_{60}\) molecule is known to form a carbon bridge at one of two possible places on the molecule: (a) across the single bond between a five member ring and a six member ring, 2, and (b) across the double bond between two fused six member rings, 3. Compounds formed by a one carbon bridge across the fused five and six membered rings are called [6,5] open fulleroids, 2, while compounds formed by a one-carbon bridge across two six member rings are called [6,6] closed methanofullerenes, 3. In this paper we report the addition of 2,4,6-cycloheptatriene across the [6,6] ring junction of the \(C_{60}\) molecule, 3. Compound 3 was synthesized in an attempt to study the stability of the cyclopropyl ring that is formed as the result of the one-carbon bridge at the [6,6] ring juncture. Compound 4 is formed when the cyclopropyl ring opens to from the cycloheptatriene cation attached to the \(C_{60}\) anion.

INTRODUCTION

The chemistry of \(C_{60}\), 1, was essentially born in 1985 with the discovery that this remarkably stable structure is formed when graphite, another form of carbon, is vaporized by laser irradiation. This research began in the spring of 1984 when Professor Harold Kroto of the University of Sussex wanted to know whether some types of carbon clusters formed in stars and might be present in interstellar space. He discussed experiments to test his hypothesis.
with Robert Curl and Richard Smalley, both of Rice University. Smalley had developed a method of forming various clusters of metal atoms produced by laser induced evaporation of the metals at very low pressure. They felt that by applying this method to graphite, the vaporized carbon produced could form clusters of carbon compounds just like in the carbon-rich stars. When they carried out the experiments in the fall of 1985, they observed small amounts of a compound present that had the molecular weight of C\textsubscript{60}. In order to confirm that indeed the compound was C\textsubscript{60} they had to isolate enough C\textsubscript{60} to apply modern spectroscopic methods to determine the structure.

The explosive growth in fullerene chemistry was stalled for the next five years awaiting a technique to produce gram quantities of the molecule for chemical and physical characterization. The technique for a large-scale preparation and purification of C\textsubscript{60} was developed in 1990 by Wolfgang Krätschmer and Donald Hoffman. With gram-scale quantities of C\textsubscript{60} on hand, the structure was soon determined and chemists from around the world began to study its physical and chemical properties. For their discovery of the C\textsubscript{60} molecule, Kroto, Smalley, and Curl were awarded the Noble prize in chemistry in 1996. However, Professor Kroto’s original hypothesis that carbon clusters are formed in stars and exist in interstellar space had not been answered. The answer came in 2000 when a team of geochemists led by Luann Becker and Robert Poreda, of the Universities of Hawaii and Rochester, respectively, reported finding C\textsubscript{60} in very old sediments that dates back to the Permian-Triassic (P–T) boundary. These sediments at the P–T boundary were deposited about 250 million years ago and this period coincides with one of the greatest mass extinction in geological history. Geologists believe that an asteroid or comet smashed into the Earth about 250 million years ago that caused debris and clouds to darken the surface of the earth and devastate the planet. This episode was similar to the well known devastation at the Cretaceous – Tertiary (C – T) boundary that wiped out the dinosaurs about 65 million years ago. The hypothesis that the impact that caused the (P – T) extinction was larger than the impact that caused the (C – T) extinction gain some support when Becker and Poreda detected some helium and argon atoms were trapped in the inner core of the C\textsubscript{60} molecules from the P–T boundary sediments. The significance of finding helium and argon trapped in the core of the C\textsubscript{60} molecules is that the isotopic ratio of helium and argon was similar to the extraterrestrial isotopic ratio. For example, the isotopic ratios of \textsuperscript{3}He/\textsuperscript{4}He in these P–T samples were about 50 times larger than the isotopic ratio of helium samples found on the earth. Finally the hypothesis of Professor Kroto had been validated. These C\textsubscript{60} molecules that formed during the explosion of stars, trapped some helium and argon atoms, and travelled on comets and asteroids through space and smashed into the surface of the earth and waited for 250 million years for scientific techniques to find them and determine where they came from. It
is interesting that chemists first synthesized this molecule in the laboratory before finding it in nature.

Our undergraduate research group is primarily concerned with the basic understanding of the chemical reactivity of this fascinating and relatively new molecule, C\textsubscript{60}. The chemistry of C\textsubscript{60} has developed into a mature discipline comprising a broad spectrum of biological and technologically fascinating compounds. Industrial application of these new compounds will have to wait for future dates.

**MOLECULAR STRUCTURE OF C\textsubscript{60}**

C\textsubscript{60}, \textbf{1}, is a truncated icosahedron (\textit{Ih}-symmetry). This is a polygon with 60 equivalent sp\textsuperscript{2} hybridized carbon atoms that show a single \textsuperscript{13}C NMR peak at 142.68 ppm.\textsuperscript{5} There are 12 five-membered rings and 20 six-membered rings in a typical soccerball-like structure.\textsuperscript{1} The molecule contains 60 single bonds with lengths of 1.45 Å and 30 1.40 Å\textsuperscript{6} double bonds. Although there are 1812 possible structures, there is only one in which all the pentagons are non-adjacent. This is the most stable and the only one that has been isolated. Because all of the double bonds are exocyclic to the pentagons, i.e. there are no double bonds within a five member ring, strain is avoided.\textsuperscript{7} The energy required to place one double bond within a five member ring has been calculated to be ca. 8.5 Kcal/mol.\textsuperscript{8}

**RESEARCH BACKGROUND**

Our current research involves the addition of one-carbon bridge moieties to the C\textsubscript{60} molecule (Figure 2). Reactions that produce such compounds are called [1,2] cycloaddition reactions. Hypothetically, there are four possible ways to add a one carbon bridge compound to C\textsubscript{60}. The [6,5] open, \textbf{2}, and the [6,5] closed, \textbf{5}, isomers should result from the addition across a [6,5] bond. Similarly the [6,6] open, \textbf{6}, and the [6,6] closed, \textbf{3}, isomers are formed from the addition across a [6,6] bond. Experimental, only the [6,5] open and the [6,6] closed isomers have been isolated. No compounds with [6,5] closed and [6,6] open structures have been reported in the literature. The isomers with the open transangular bonds (\textbf{2} and \textbf{6}) are called fullerioids, while those with closed transangular bonds (\textbf{3} and \textbf{5}) are called methanofullerenes. Computational studies have shown that the [6,5] closed and [6,6] open isomers have very high strain energy and are unstable because they contain two and three double bonds respectively with their five member rings.\textsuperscript{9} The [6,5] open fullerioid isomer, such as compound \textbf{7}, (Figure 3) is called the kinetic product because it always forms faster then \textbf{8}, while \textbf{8} is called the thermodynamic product because it is the more stable product formed at high temperature. Compound \textbf{7} has been isolated and is reported to rearrange to the corresponding [6,6] closed methanofullerene isomer, \textbf{8}, by several mechanisms: (a) heating in the dark, via thermal first order rearrangement (b) in the presence of light, via a photochemical zero-order rearrangement and (c) in the presence of
a catalyst, such as, tetracyanoethylene (TCNE). When groups that can stabilize a radical or a cation on the methano-bridge carbon, such as 7, are present the rearrangement has been shown to be very fast. The rearrangement from 7 to 8 in the presence of TCNE had been postulated to rearrange thermally by a zwitterionic-type intermediate similar to compound 4.

The purpose of this research project was to answer two fundamental questions about fulleroids, 2, and methanofullerene, 3 compounds. (1) Are the [6,5] open fulleroids, such as 2,4,6-cycloheptatriene–C\textsubscript{60}, 2, stable enough to be isolated at room temperature or do they undergo rapid rearrangement to the [6,6] isomer, 3? (2) Is the [6,6] closed methanofullerene, 3, stable enough to be isolated at room temperature or will the cyclopropyl ring open to form compound 4? In this study we report that the [6,5] open fulleroid, 2, could not be isolated at room temperature because the rearrangement of the [6,5] open fulleroid, 2, to the corresponding [6,6] methanofullerene isomer, 3, is very fast. This rearrangement occurs under the reaction conditions. Second, [6,6] closed methanofullerene, 3, is very stable at room and does not appear to form the zwitterionic salt, shown as compound 4 under our current experimental conditions.

RESULTS AND DISCUSSIONS

In order to examine both the stability of [6,5] open fulleroid, 2, and the stability of the cyclopropyl ring in [6,6] closed methanofullerene, 3, we designed a synthetic scheme to make these cycloheptatriene–C\textsubscript{60} derivatives starting from tropone, compound 9 (Scheme 1). The troponetosylhydrozone, 12, was synthesized by converting tropone, 9, to 7,7-dichlorocycloheptatriene, 10, followed by the reaction of the gem-dichloride with p-toluenesulfonhydrazine. In order to synthesize 7,7-dichlorocycloheptatriene, 10, tropone, 9, was added dropwise to an excess of thionyl chloride at 0 °C. Troponetosylhydrozone salt, 11, was prepared by refluxing p-toluenesulfonhydrazide with 7,7-dichlorocycloheptatriene, 10, in ethanol for 30 min and the deep red cycloheptatriene tosylhydrazone salt, 11, was recrystallized easily in ethanol. The cycloheptatriene tosylhydrazone salt, 11, was then dissolved in dichloromethane and methyllithium was added. A toluene solution of C\textsubscript{60} was added to the reaction mixture. The mixture was protected from light and refluxed for 15 min to give compound 3. In the 1\textsuperscript{H} NMR spectrum of compound 3 all the peaks occur in the double bond region of the spectrum (Figure 5). In mass spectrum of compound 3, the mass to charge ratio is 810 corresponds to the molecular ion peak (Figure 6). The data for the 13\textsuperscript{C} NMR spectrum of compound is given in the experimental section. According to the 1\textsuperscript{H} and the 13\textsuperscript{C} NMR spectra there is no evidence for the [6,5]
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open isomer, 2, in which case the sp² hybridized proton that is over the five
membered ring would occur further down field. Given the fact that [6,5] open
fulleroid, 2, was not isolated, we postulate that it rearranges rapidly under the
reaction conditions. Compounds that can stabilize a radical or cation on the
methano-bridge carbon and have their π-orbitals arrange parallel to the cage
as is the case with compound, 2, tend to arrange quickly to the corresponding
thermodynamic [6,6] closed isomer such as, 3. It appears that 2 rearranges
to 3 so rapidly that we could not isolate at it room temperature. In the ¹³C
NMR spectrum of compound 3, the methano-bridge carbon occurs at 50.8
ppm while the bridgehead carbons occur at 81.5 ppm. This is characteristic of
the [6,6] closed isomer.

Compound 4 presents a very interesting case. C₆₀ is a fairly good electron
acceptor and is known to form stable anions. Even though cycloheptatriene
is not aromatic, cycloheptatrienyl cation (tropylium cation) is a Hückel (4n +2)
system and is a very stable aromatic cation, as demonstrated in the formation
of tropylium bromide. Given that both the cycloheptatrienyl cation and the C₆₀
anion are both relatively stable in other systems it will be interesting to see
if we can observe the reaction from 3 to 4 for the reasons discussed above.
We have, thus far, not been able to confirm the formation of compound 4.
Compound 3 is soluble in non-polar solvents and insoluble is polar solvents
like CHCl₃, DMSO and H₂O. The opposite will be the case for compound 4.
It is expected to be soluble in polar solvents, such as, DMSO or possibly H₂O
and insoluble in nonpolar solvents like benzene and hexane.

The cyclopropyl ring in compound 3 appears to be very stable. However, we
may be able to find a reagent to catalyze the ring opening from compound 2 to
3. Our future research approach is to attempt to form the cycloheptatriene-C₆₀
zwitterion in the presence of electron acceptors, such as, tetracyanoethylene
(TCNE). TCNE has been shown to induce the rearrangement for some types
such as TCNE may induce the ring opening of 3 to form the zwitterions 4. We
are also in the process of doing some collaboration with another colleague
with regard to theoretical calculations to determine the energy barrier in the
reaction from 3 to 4. It will be very interesting to determine how large this
barrier is, if there is one.

CONCLUSION

These results demonstrate the 2,4,6-cycloheptatriene-C₆₀[6,5] open
fulleroid, 2, is very unstable and rearranges under the reaction conditions to
the corresponding [6,6] closed methanofullerene isomer, 3. In addition, the
cyclopropyl ring in 2,4,6-cycloheptatriene-C₆₀[6,6] closed methanofullerene,
3, appears to be very stable. We did not observe the ring opening to form the
cycloheptatriene-C₆₀ zwitterion, 4. Further experiments will be conducted with
the goal of synthesizing compound 4 by reacting compound 3 with TCNE.

**EXPERIMENTAL SECTION**

**Instrumentation and Materials:**

The NMR spectra of ¹H and ¹³C NMR were recorded on Bruker AC 250 spectrometers using dichlorobenzene-­d₄ (ODCB-d4) and 1:2 CDCl₃:CS₂ as solvents. FAB mass spectra were measured on a VG 7070 spectrometer with m-nitrobenzylalcohol (NBA) as the matrix. Commercial reagents were used as received from Aldrich. Solvents were distilled before use. Fullerene 60 (99.5%) was purchased from MER Corporation. Reactions were monitored by thin-layer chromatography (TLC) using 13181 silica gel with fluorescent indicator. Flash column chromatography was performed using 60-200 mesh Fisher silica gel. Yields refer to chromatographically and spectroscopic (¹H and ¹³C NMR) homogeneous materials.

**Preparation of the Stock Solution of C₆₀.** A soxhlet extractor was used to prepare the stock solution of C₆₀ in dry toluene. Toluene (500 ml) was placed in a 1000 ml flask mounted on a soxhlet extractor. Pure C₆₀ (0.51 g) was placed in a U-shape, filter paper thimble. The toluene solution was refluxed for 1 to 2 days until all of the C₆₀ went into solution. The C₆₀ stock solution was stored in a flask sealed with a glass stopper and wrapped with aluminum foil to prevent exposure to ambient light.

**Preparation of 7, 7- dichlorocycloheptatriene (Compound 10).** 7, 7- dichlorocycloheptatriene was prepared by the method of Jones and Ennis.¹¹ Tropone (1.34 g, 12.6 mmol) was added dropwise to excess thionyl chloride (1.34 mL) at 0 °C. Thionyl chloride was both the solvent and the halogenating agent. After all of thionyl chloride had been added, the reaction mixture was refluxed gently for 5 min on a steam bath. The excess thionyl chloride was removed, using a rotary evaporator to yield the yellow crystalline solid 7, 7- dichlorocycloheptatriene. It was used in the next step without further purification.

**Preparation of 2,4,6-cycloheptatriene tosylhydrazones hydrochloride salt**¹¹ (Compound 11) A solution of 450 mg (2.42 mmol) of p-toluenesulfonylhydrazine in 5 mL of absolute ethanol was added quickly to a well stirred solution containing 304 mg (2.45 mmol) of 7, 7- dichlorocycloheptatrienone, 10, dissolved in 5 ml of ethanol. The dark red solution was quickly stirred at room temperature for 35 min. The yellow solid was filtered and washed with ether.

**Preparation of 2,4,6-cycloheptatriene tosylhydrazones**¹¹ (compound 12). To a stirred mixture of 50 mL of 10 % NaHCO₃, a solution and 25 mL of dichloromethane was added 1.00 g (3.22 mmol) of compound 11. Two layers separated after 20 minutes. The aqueous layer was washed two times with 10 mL portions of dichloromethane. The organic fractions were combined, washed, and dried with magnesium sulfate. The solvent was removed using a rotary evaporator to give a dark red solid in about 0.796 g (90% yield). ¹H NMR
The Synthesis and Characterization of 2,4,6-Cycloheptatriene-C$_{60}$[6,6] Closed Methanofullerene (CDCl$_3$, 250 MHz): $\delta$= 2.1 (s, 1H), 2.12 (s, 3H), 6.5 (m, 6H), 7.3 (d, 2H), 7.8 (d, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$= 155.7, 143.9, 136.8, 135.3, 134.2, 134.0, 130.5, 130.3, 129.4, 128.1, 124.5, and 21.5.

Preparation of 2,4,6-cycloheptatriene-C$_{60}$.$^{10}$ (compound 3). To a solution of tosylhydrazone (0.1 mmol) in 3 ml of hexane at 0 °C under N$_2$ in a 250 ml flask was added MeLi (1.4 M, 0.107 ml, 0.15 mmol) using a syringe. A previously prepared C$_{60}$ solution in toluene (72 ml, 1.40 mM, 0.1 mmol) was added to the flask. The flask was heated at reflux for 20 to 30 min and monitored by TLC in toluene or hexane:toluene (4:1). The solvent was reduced in using a rotary evaporator to 20 ml which was then loaded on a silica gel column and eluted with toluene or hexane:toluene. The yields were 40 %. $^1$H NMR (ODCB-$d_4$, 250 MHz): $\delta$= 7.2 – 6.4 (m, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$= 149.0, 147.3, 146.8, 146.0, 145.0, 144.9, 144.2, 144.0, 143.8, 143.5, 143.2, 142.9, 142.8, 141.9, 141.0, 140.8, 140.3, 140.2, 139.9, 139.1, 138.6, 137.7, 136.6, 134.4, 132.1, 131.1, 130.9, 130.0, 129.7, 81.5, 50.8. FABMS (NBA): m/s 810 ((M+1)$^+$), 720 (C$_{60}^+$).  

WORKS CITED


**FIGURE 1:** A probably pathway for the formation of cycloheptatriene cation-C60 zwitterion

**FIGURE 2:** Four hypothetical ways for cycloheptatriene to form one carbon-bridge compounds to C60.
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FIGURE 3: Rearrangement of [6,5] open fulleroid to [6,6] closed methanofullerene

FIGURE 4. The $^1$H NMR spectrum of 2,4,6-cycloheptatriene p-toluenesulfonhydrazone, compound 12, recorded in CDCl$_3$.

FIGURE 5. The $^1$H NMR spectrum of 2,4,6-cycloheptatriene-C$_{60}$[6,6] closed methanofullerene, compound 3, recorded in 1,2-dichlorobenzene-d$_4$. 
FIGURE 6: The mass spectrum of 2,4,6-cycloheptatriene-C$_{60}$ [6,6] closed methanofullerene, compound 3.