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Synthesis of 3,5-dimethoxyphenyl-1-methyl C_{60} [6,5] Open Fulleroid and its Diasteriometric Isomer, [6,6] Closed Methanofullerene

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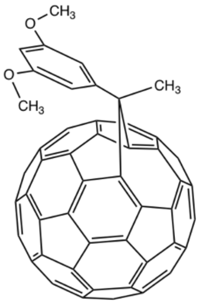
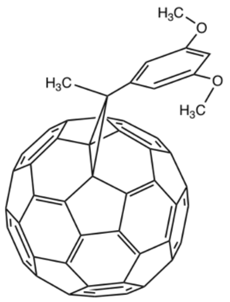
Abstract



[6,5] Open



[6,6] Closed

The addition of a one-carbon bridge across the double bond on the C_{60} fullerene molecule can theoretically form one of four possible isomers. These isomers are formed from open and closed bonds between the five and six membered rings on the fullerene surface. In this paper we report the synthesis of 3,5-dimethoxyphenyl-1-methyl C_{60} [6,5] Open Fulleroid and its diasteriometric isomer, [6,6] Closed methanofullerene. Our experimental results indicate that compound **2,** with the methoxy group over the five-membered ring, was isolated as the predominate isomer and it undergoes complete rearrangement to **4** when heated in ambient light.

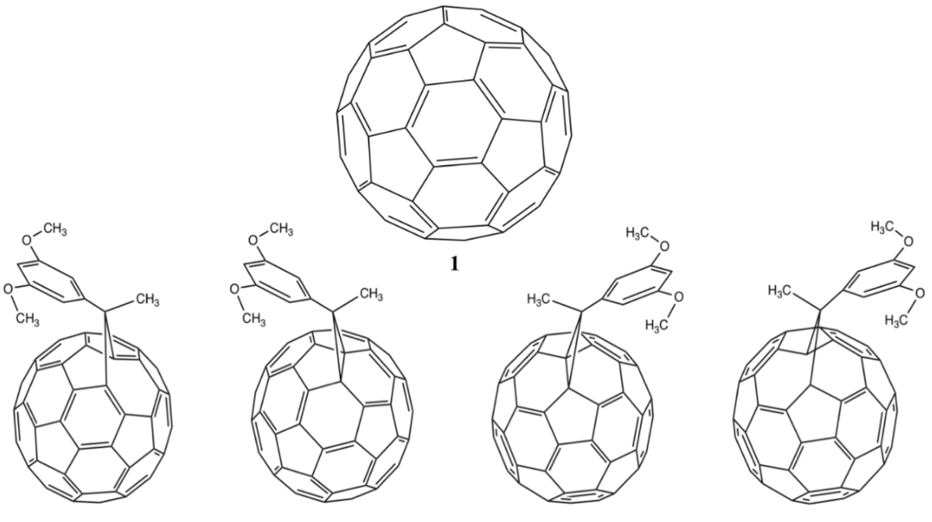
Introduction

Molecular carbon has three known allotropes. Two of these allotropes, graphite and diamond, are very well known and understood. However, in 1984 Harold Kroto and his team at the University of Sussex speculated on a new allotrope while studying infrared spectra of stars. Later experiments[1] led to the synthesis and characterization of the third allotrope of carbon, the C_{60} molecule, with 60 carbon atoms resembling the shape of a soccer ball shown in Figure 1. NMR data confirmed the structure of C_{60} as that of a cage-like molecule, looking very much like a soccer ball with 12 five member rings being surrounded by 20 six member rings. Kroto and his co-workers called this C_{60} molecule buckminster fullerenes after the famous designer of geodesic domes, Buckminster

Figure 1: A molecule of C_{60}.

Fuller. Since then many other sizes of fullerene (C_{70}, C_{80}) cages have been isolated. There are many possible resonance structures for C_{60} but the only stable form that has been isolated is that shown in figure 1, where every double bond is inside of a six-membered ring. Placing a double bond in the five member ring introduces additional strain in the curved molecule.

The structure of C_{60} was initially thought to be aromatic due to it 4n+2 pi electron system, according to Huckle's rule. Aromatic systems are generally very stable and have low reactivity towards reagents that react with alkenes. The C_{60} molecule has been reported to react more like regular alkenes and unlike those of aromatic compounds.[1c] In addition, C_{60} is fairly electrophilic making the additions across any one of its many double bonds a relatively simple process. The addition of a one carbon (methano) bridge across a double bond on the fullerene cage can theoretically lead to one on four possible isomers as seen in Figure 2. However, only compounds similar to **2** and **4** have been



[6,5] Open
2

[6,5] Closed
3

[6,6] Closed
4

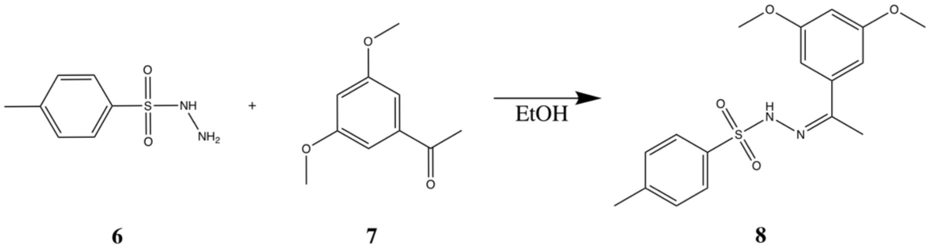
[6,6] Open
5

Figure 2: Possible isomers when a one carbon bridge is added across a double bond of C_{60}. Only **2** and **4** have been observed in experimentally.[1d] The addition of a methano bridge via a hydrazone has been

reported to produce the [6,5] open isomer as the kinetic project. Upon heating, the [6,5] isomer rearranges to the corresponding [6,6] closed isomer.[2a] Similar rearrangement has been reported to proceed through a biradical intermediate with zeroth order kinetics when catalyzed by light, and first order kinetics when heated in the dark.[2,3] Nuclear magnetic resonance (NMR) can be used to study this rearrangement by monitoring the chemical shifts of the methyl peaks. In this study, we report that the compound **2** was synthesized and upon heating it completely rearranged to **4**. The chemical shifts of the methyl group in ^{1}H NMR spectrum was used to help characterized the products and monitor the rearrangement.

Results and Discussion

The reaction mixture, shown in scheme 1, between p-toluenesulfonhydrazide, **6,** and 3,5-dimethoxyacetophenone, **7**, was refluxed in ethanol for 5 hours and recrystallized to produce a tosylhydrazone, **8,** as clear white crystals in 57% yield. The reaction mixture was monitored using silica getl thin layer chromatography (TLC). Compound **8** is more polar than **6** and **7** so its TLC spot appeared lower on the TLC plate.



Scheme 1: The reaction mixture between p-toluenesulfonhydrazide, **6**, and 3,5-dimethoxyacetophenone, **7**, was refluxed in ethanol for 5 hours and recrystallized to produce a tosylhydrazone, **8,** in 57% yield.

This difference in polarity allowed us to monitor the reaction with TLC plates. Compound **8** was recrystallized in methanol and air dried using a Buchner funnel.

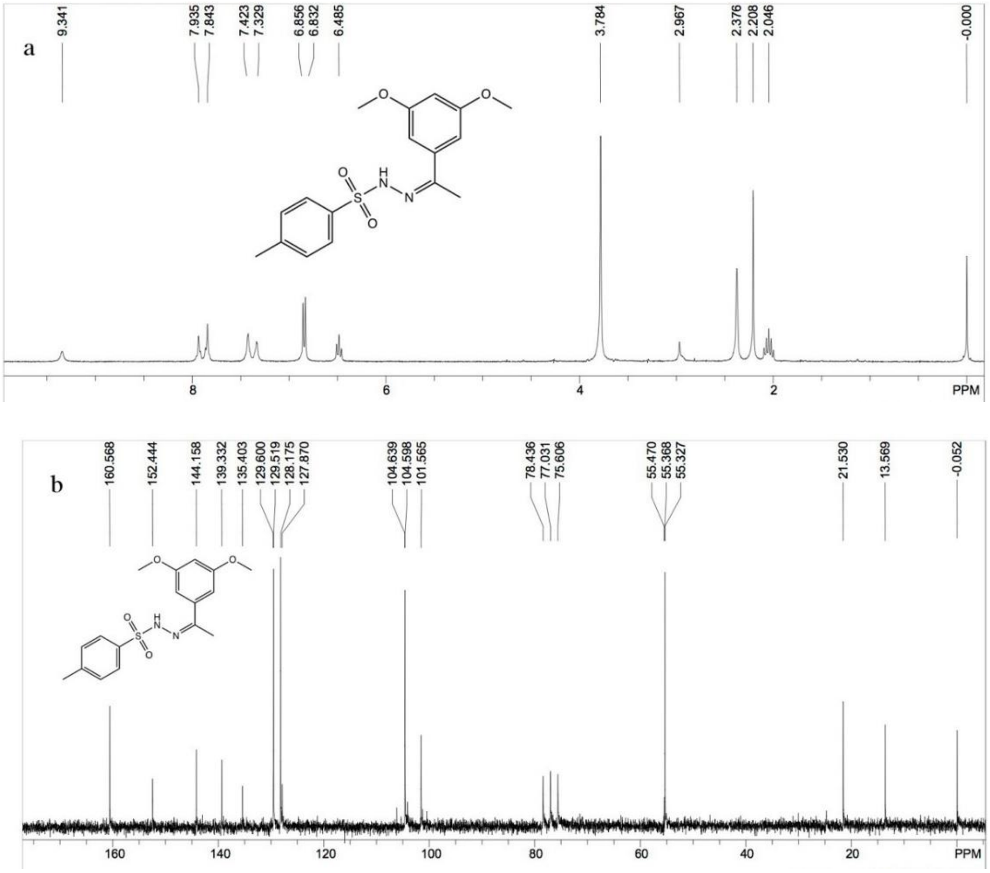
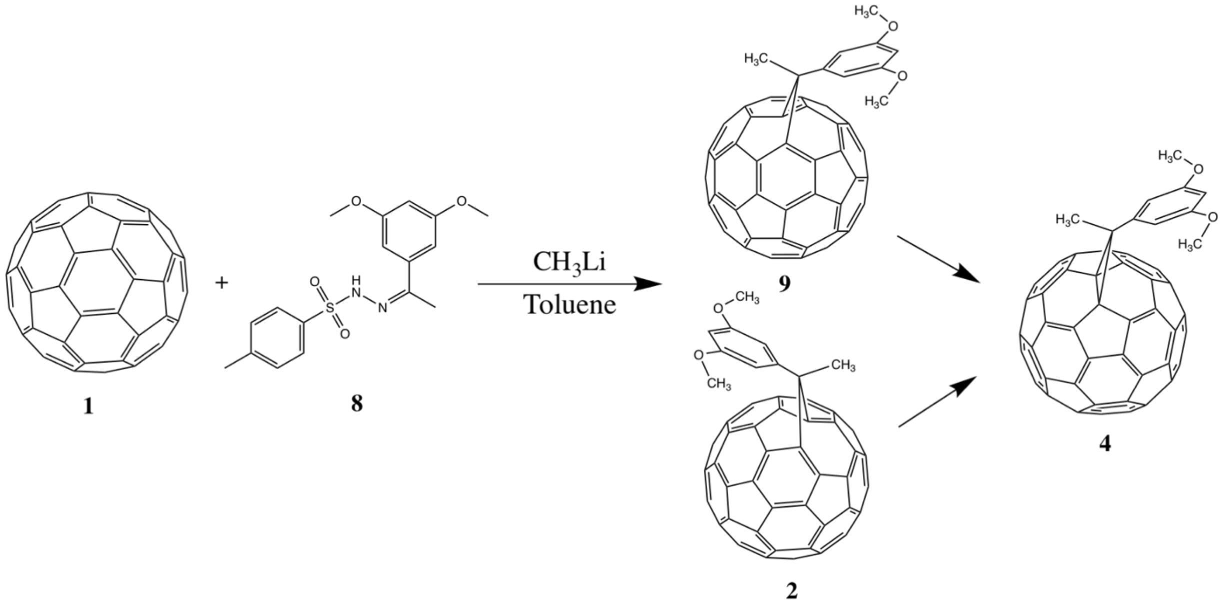


Figure 3: **a.)** The ^{1}H NMR of compound **8** in acetone-*d6*. **b.)** The ^{13}C NMR of compound **8** in chloroform-d. Both spectra were obtained using an Anasazi ETS 90 MHz instrument.

The proton (^{1}H) NMR spectrum of compound **8** is shown in Figure 3 (a). The ^{1}H NMR showed the methoxy peaks at δ 3.784 and the methyl peak at δ 2.37 are in in a 2:1 ratio. The second methyl peak in the 1H NMR occurs at δ 2.20. The ^{13}C NMR shows all of the 12 peaks. Both of ^{1}H and ^{13}C NMR spectra data are consistent with the structure of compound **8**.

Compound **8** was dissolved in 20 mL of hexane in a 250 mL round bottom flask and the temperature brought to 0 °C in an ice bath. The methyl Lithium, dissolved in hexane, was added to the cold solution of compound **8**. The C_{60}, previously dissolved in toluene was added to cold solution of compound 8 and methyl lithium. The reaction mixture was then refluxed and monitored using TLC (Scheme 2). The refluxing was terminated after 45 minutes when a second product spot appeared. This second spot is believed to be side products with multiple adducts. The products are more polar than C_{60} and appeared as a lower spot on the plate. Initially the silica gel column was run using pure toluene as a mobile phase due to the fact that a toluene TLC showed adequate separation with distinct, concise spots. However, separation in the column itself was somewhat poor with significant intersection between the two fractions. Later a repeat of the separation was performed with a 3:1 toluene/hexane mobile phase that showed some improvement in separation. The poor separation indicated that the reaction mixture contained unreacted C_{60} in addition to the desired product. The three possible isomers seen in Scheme 2 cannot be separated by column chromatography. Isomers present will exist as a mixture in the final product.

Scheme 2: The reaction of 1 with 8. Three possible isomers can be generated from this reaction: **2**, **4**, and **9**



The ^{1}H NMR spectrum of the product of reaction **8** with C_{60}, shown in figure 4, is consistent with compound **2.** There are no peaks consistent with compound **9**. These two possible kinetic products of this reaction, **2** and **9**, can be distinguished by the methyl group above a five membered or six membered ring. Each will result in a different ^{1}H NMR chemical shift. Prato et al [2] report that when the methyl group sits above a five member ring the peak will appear at δ 3.19.

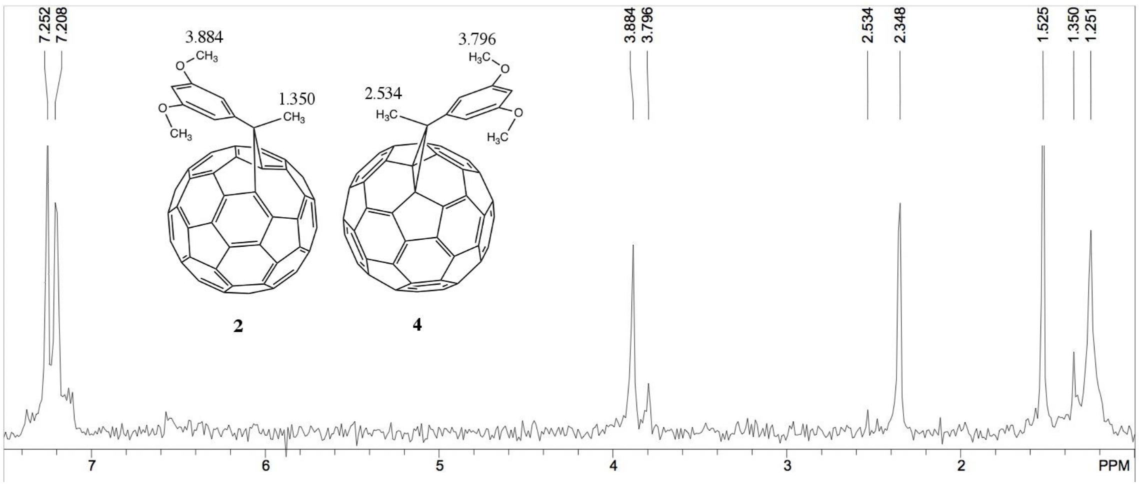


Figure 4: The proton NMR of the product mixture shows compound **2**, methyl group at δ 1.35 and the methoxy groups at δ 3.85, as the predominate isomer. There are traces of compound **4**, with methyl group at δ 2.53.

If, however, the methyl group sits above a six member ring the peak it appears around δ 1.32.[2] Since the methoxy proton peak appears around δ 3.7-4.0 regardless of which ring it sits above we must use the methyl peak for analysis. Figure 4 shows the methyl peak does in fact appear at δ 1.3 indicating that **2** is the predominate isomer. The absence of a methyl peak at peak at δ 3.1 provides no evidence to compound **9**.

There is also a small peak at δ 2.534 . Prato et al reports the methyl peak of the [6,6] closed isomer to appear at δ 2.52;[2] meaning that Figure 4 indicates the presence of **4** as well as **2**. We can pair these methyl peaks to their corresponding methoxy peaks by the ratio of their heights. Since there are 6 methoxy protons and only 3 methyl protons meaning the peaks should exists as a 2:1 ratio of heights. Using this ratio we can conclude that the peak at δ 3.884 corresponds to **2** and the peak at δ 3.796 corresponds to **4**.

The NMR evidence in Figure 4 indicates that **2** is the major product. The reason for this can be explained by Schick and Hirsch's paper. They suggest the mechanism proceeds through a pyrazoline intermediate.[5] It was suggested that the diazo detaches from the methano bridge carbon before leaving as molecular nitrogen. The diazo adduct provides temporary steric hinderance over the six-membered ring causing the larger group to rotate away from it. This is why we see the methoxy group over the five-membered ring as our major product. Had the larger group rotate toward the diazo group and positioned itself over the six membered ring the methyl peak would instead appear at δ 3.1 and generate 9.[2]

Heating the reaction mixture of compounds **2** and **4** in ambient light induced the rearrangement of **2** to yield a single isomer, the [6,6] closed, compound **4**.[3] Evidence for this can be found in Figure 5. Noting that the methoxy peak at δ 3.884 as well as the methyl peak at δ 1.350 disappear. This leaves only one peak in the methoxy range indicating the presence of a single isomer. The small methyl peak at δ 2.534 from **4** (Figure 4) has grown in proportion with the methoxy group as further evidence of the conversion.

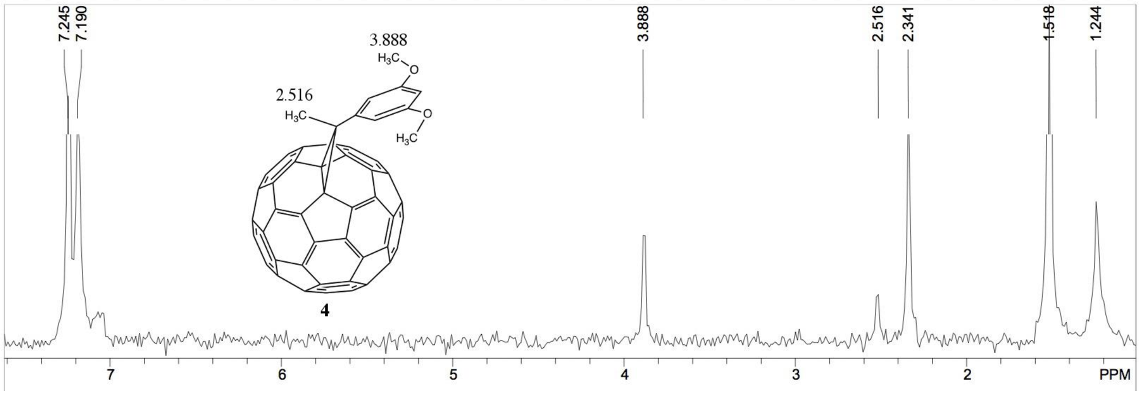
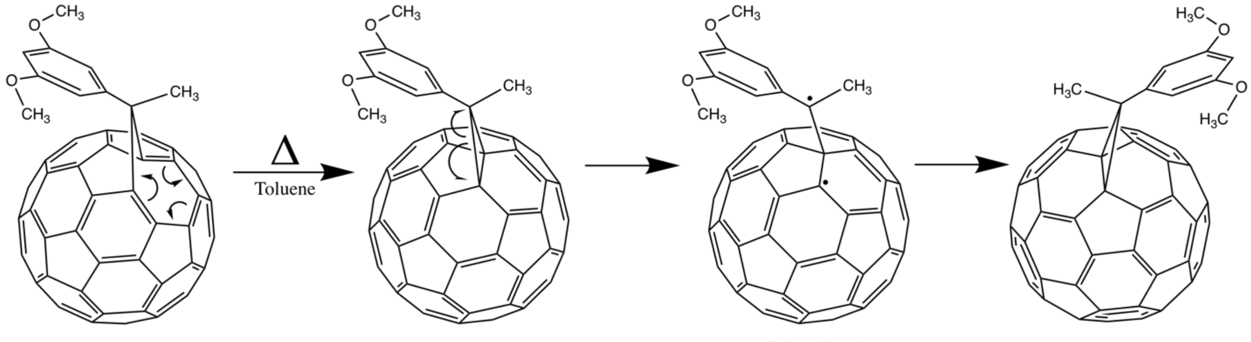


Figure 5: ^{1}H NMR spectrum of compound **4**. The mixture of compound **2** and **4** was refluxed in toluene overnight. This spectrum shows a complete rearrangement of **2** to **4**.

Hall et al found this rearrangement to proceed through a biradical intermediate as seen in Scheme 3.[3] The resonance structures of the biradical can be drawn is such a way that moves the radical species to carbon at a junction of two six membered rings; at which point the bridge will close creating **4**. This mechanism proceeds with heat and can be catalyzed by light. A plausible mechanism in scheme 3 below accounts for the complete rearrangement of **2** to **4**, via a biradical intermediate.



2 **3** **Biradical** **4**

Scheme 3: The [6,5] open isomer, 2, rearranges to the [6,6] closed isomer, **4**, through a biradical intermediate.

The presence of **4** in the initial product mixture is likely due to the rearrangement taking place while the reaction was being refluxed. However, the formation of **4** by another mechanism cannot be ruled out entirely. Figure 6 shows the overlay of ^{1}H NMR spectrum before and after the refluxing overnight. The growth of the methyl peak at δ 2.515 is clearly shown. This spectra providence evidence for the full rearrangement of when heated again under lighted. Figure 6 shows the change in the spectra before and after the mixture of **2** and **4**. The peak at δ 2.515 in Figure 5 and 6 provides evidence for the presence of compound **4**. The ^{13}C spectrum would surely strengthen this evidence.

In order to gather further evidence of the isomerism of the product and its rearrangement ^{13}C NMR was attempted. Initially the NMR data was collected for over the span of 10-12 hours using chloroform-d as a solvent. Due to the limited solubility of the compound in chloroform-d the it failed to remain in solution for the duration of the test; leading to poor signal to noise ratio. There was considerable improvement when the solvent was switched to o-dichlorobenzene-d4. We also lengthened the duration of the data collection to 48 hours. However, as can be seen in Figure 7, the only discernible peak (aside from the solvent peaks at δ 125-135) is located at δ 142.777. This peak is indicative of unreacted C_{60}. The presence of C_{60} in the product mixture is due to the poor separation in the silica gel column.

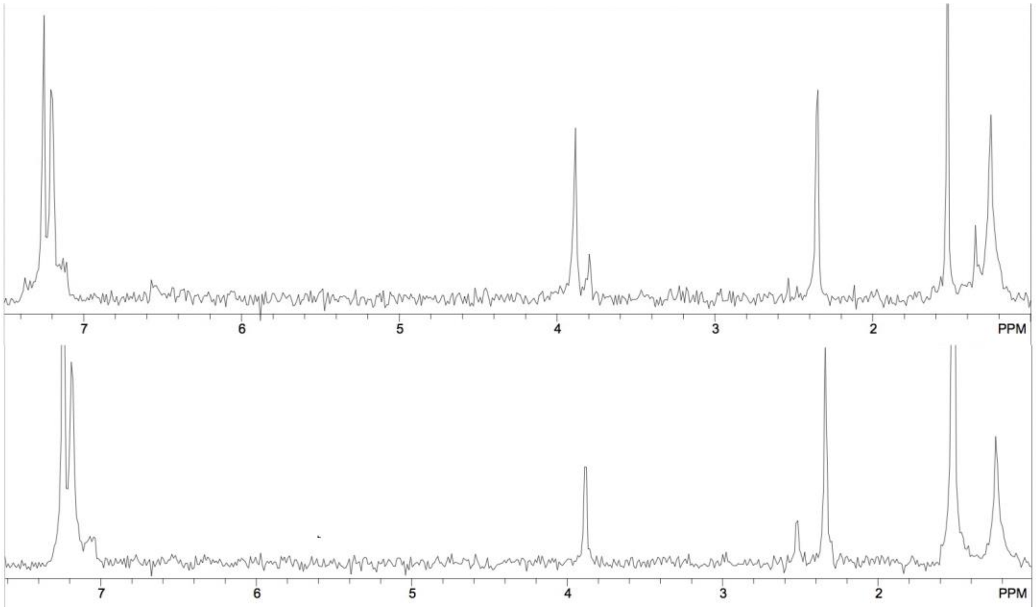


Figure 6: The top ^{1}H NMR spectrum was generated from the reaction mixture containing both **2** and **4**. The bottom spectrum was generated after heating overnight in toluene. The methyl peaks for compound **2** are gone and the peaks for compound **4** are evident. See the above discussion for the location of the methyl and methoxy peaks.

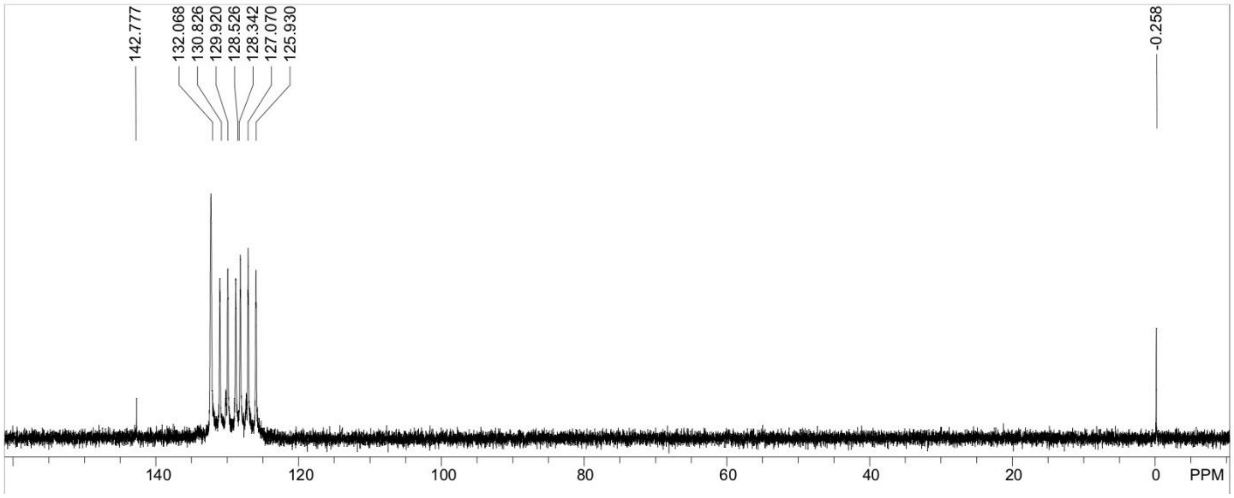


Figure 7: ^{13}C NMR of the reaction mixture contains only the C_{60} peak at δ 142 .

Though many improvements were made as scan parameters and procedures were fine-tuned, we were unable to generate useful ^{13}C NMR data. Carbon-13 only 1% of naturally occurring carbon so the probability of any one of the seventy carbon atoms being the desired isotope is very low. In addition, the low solubility of our compounds produced further challenges as it reduced the overall number of molecules that could be scanned by the instrument. Figure 7 does show promise, however. The fact that we were able to successfully obtain ^{1}H NMR data of the product while Figure 7 shows only the C_{60} peak at δ 142 probably indicates that the product is present it is a much lower amount that the unreacted C_{60} in the sample. There is still a possibility that running scans for upwards of 48 hours may allow us to lower the noise enough to see our expected peaks. It is our hope that better chromatography parameters will improve our product's separation from any unreacted C_{60} reducing its influence in the ^{13}C NMR.

Conclusion

The reaction of C_{60} with compound **8** produced compound **2**, the [6,5] open isomer, as the major product of the reaction while compound **9** was not observed. While compound **4** was present in the reaction mixture it likely formed via rearrangement of **2** while the reaction was still running rather than forming through a unique mechanism. Compound **2** was also found to rearrange completely to compound **6** when heated and exposed to light. Evidence of this rearrangement was consistent with ^{1}H NMR data.

Experimental

Materials

3,5-methoxyacetophenone, **6**, and p-toluenesulphonhydrazide, **7**, as well as C_{60}, **1**, were obtained from Sigma-Aldrich. NMR solvents were obtained from Cambridge Isotope Laboritories Inc. and Acros. NMR spectra were taken with an Anasazi ETS 90MHz instrument.

Preparation of C_{60} Stock Solution

C_{60} (.51 g) is placed in a paper thimble inside of a soxlet extractor. 500 mL of toluene is placed into a 1 L round bottom flask and connected to the soxlet extractor. The toluene is refluxed through the extractor for 24 hours in order to fully dissolve the C_{60}. The flask containing the 1.4 mM solution is then parafilmed and wrapped in aluminum foil.

Synthesis of 3,5-methoxy-1-methyltosylhydrazone (**8**)

Compounds **6** and **7** were placed into a 250 mL round bottom flask in a 1:1.2 molar ratio along with 50mL of ethanol. The solution was then refluxed under constant stirring for

4 hours and monitored by TLC [2.184g, 57% yield]. ^{1}H NMR (C_3D_6O, 90 MHz): δ 2.208 (s, 3H), 2.376 (s, 3H), 2.967 (s, 1H), 3.784 (s, 6H), 6.485 (t, 2H), 6.832 (d, 2H), 7.329 (d, 2H), 7.843 (d, 2H), 9.341 (s, 1H). ^{13}C NMR ($CDCl_3$, 90 MHz): δ 13.569, 21.530, 55.368, 101.565, 104.598, 127.870, 129.519, 135.403, 139.332, 144.158, 152.444, 160.568.

Synthesis of 3,5-methoxy-1-methyl Fulleroid

Compound **8** (.035 g) was dissolved into 3 mL of hexane in a 250 mL round bottom flask and cooled to 0 C°. Methyl lithium (.1 mL) is added to the solution as well as 72 mL of C_{60} stock solution. The reaction was refluxed for 45 minutes and monitored with TLC. The product mixture was separated by silica gel column in a toluene mobile phase. The compound powder was placed into a vile and covered with foil to protect it from ambient light. This reaction, Scheme 2, can produces three possible isomer: **9**, **2**, and **4**. (.036 g, 45% yield) ^{1}H NMR ($CDCl_3$, 90 MHz): [6,5] open isomer δ 1.350 (s, 3H), 3.884 (s, 6H), 7.208 (s, 2H), 7.252 (s, 1H). [6,6] closed isomer δ 2.534 (s, 3H), 3.796 (s, 6H), 7.208 (s, 2H), 7.252 (s, 1H).

Rearrangement from **2** to **4**

A small amount of reaction mixture is dissolved in 40-50 mL of toluene in a 250 mL round bottom flask. The solution is refluxed for 18-24 hours with the light in the fume hood left on as the reaction is catalyzed by light. The solvent is then drawn off using arotary evaporator. [6,6] closed isomer δ 2.516 (s, 3H), 3.888 (s, 6H), 7.190 (s, 2H), 7.245 (s, 1H).

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