

# Methylated and phenylated C<sub>60</sub> from fluorinated fullerene precursors

E.T. Mickelson, R.H. Hauge, J.L. Margrave\*

Department of Chemistry and Rice Quantum Institute, Rice University, MS 60, 6100 Main Street, Houston, TX 77005, USA

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## Abstract

C<sub>60</sub> has been fluorinated with F<sub>2</sub> to yield a product which consists mostly of C<sub>60</sub>F<sub>44</sub>. This species was then reacted with methyl and phenyl lithium reagents to yield the respective methylated and phenylated nucleophilic substitution products. These products have been confirmed and characterized by IR, <sup>1</sup>H-NMR and mass spectroscopies. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Since the discovery of C<sub>60</sub> [1] there have been many studies done on the products of the heterogeneous reaction between it and F<sub>2</sub> [2–5]. It is generally believed that a maximum of 48 fluorines may be added to a single C<sub>60</sub> cage without resulting in the cleavage of carbon–carbon sigma bonds [6]. This is despite theoretical predictions of a stable C<sub>60</sub>F<sub>60</sub> species [7].

The reaction between fluorinated C<sub>60</sub> and a variety of alkyl lithium reagents has been investigated before [8]. In this case, the rates of reaction were followed by monitoring fluorine loss in an NMR tube using <sup>19</sup>F-NMR. While the authors speculated that a frontside nucleophilic attack might lead to substituted products, no product isolation or further analysis was carried out on the products.

In another report [9], phenyl lithium was added to C<sub>60</sub>F<sub>44–46</sub>. It was observed that large amounts of biphenyl were produced along with smaller amounts of fluorobenzene. No mention was made of any phenylated C<sub>60</sub> species that might have been present among the product species.

While both methylated [10] and phenylated [11–13] C<sub>60</sub> species have been produced and well-characterized, they have both been made using synthetic routes different than those presented here. Here we demonstrate that alkylating fullerenes by way of the nucleophilic substitution (using an alkyl lithium reagent) of a fluorinated fullerene precursor is a viable option for the synthesis of these interesting molecules.

## 2. Experimental

### 2.1. Preparation of the fluorinated C<sub>60</sub>

C<sub>60</sub> (Southern Chemical Group, LLC – 99.5% purity) was fluorinated in a monel flow reactor at 260°C with a mixture of F<sub>2</sub> (Air Products 98%) diluted in helium (Trigas 99.995%). HF was removed from fluorine by passing it through an HF trap (Matheson Gas Products) containing sodium fluoride pellets. Flow rates for the F<sub>2</sub> and He were 4 and 20 sccm, respectively. Fluorination times lasted for approximately 16 h. The white fluorinated product was characterized by EI mass spectroscopy (Finnigan MAT 95) and yielded a mixture of products of mostly C<sub>60</sub>F<sub>44</sub> with smaller amounts of C<sub>60</sub>F<sub>42</sub> and C<sub>60</sub>F<sub>46</sub>.

### 2.2. Preparation of the methylated C<sub>60</sub>

Methyl lithium (1.4 M in diethyl ether, Aldrich) was added in molar excess via syringe to a flask containing ~100 mg of fluorinated C<sub>60</sub>. The mixture was then refluxed under an inert atmosphere (with stirring via a PTFE magnetic stir bar) for 3 h. After 3 h time the methyl lithium was neutralized by injecting a mixture of methanol and diethyl ether into the flask. The product was filtered to remove most of the LiOH/LiF/LiOCH<sub>3</sub> formed. The filtrate was then placed in an evaporating dish where the solvent was allowed to evaporate. The product was then re-dissolved in toluene and any remaining LiOH/LiF/LiOCH<sub>3</sub> was extracted from it with water in a separatory funnel.

\*Corresponding author.

### 2.3. Preparation of the phenylated $C_{60}$

Phenyl lithium (1.8 M in 70 : 30 cyclohexane/ether, Aldrich) was added to the fluorinated  $C_{60}$  in the same manner as with the methylation. The mixture was stirred at room temperature for 1 h. The mixture was stirred at room temperature for 1 h. The residual phenyl lithium was then neutralized with a mixture of methanol and ether. The product was filtered and the solvent removed from the filtrate. The product was re-dissolved in toluene and residual LiOH/LiF/LiOCH<sub>3</sub> was extracted from it using water in a separatory funnel. The toluene was then evaporated and biphenyl was removed from the resulting residue by heating it in a stream of nitrogen inside a tube furnace for 1 h at 300°C.

The methylated and phenylated  $C_{60}$  products were both characterized by the following: EI mass spectroscopy (Finnigan MAT 95), IR spectroscopy in a KBr matrix (Perkin-Elmer Paragon 1000 FTIR) and <sup>1</sup>H-NMR spectroscopy in CDCl<sub>3</sub> (Bruker Advance 200 FT-NMR).

## 3. Results

### 3.1. Methylated $C_{60}$

The methylated product is orange in color and it is very soluble in non-polar organic solvents. It is apparently quite

stable in air for long periods of time. The EI mass spectrum of the methylation product is shown in Fig. 1. While the most abundant peak is from a  $C_{60}(\text{CH}_3)_{21}$  species, the spectrum shows a number of methylation products  $C_{60}(\text{CH}_3)_n$  where  $n$  ranges from 1 to 28.

The IR spectrum is shown in Fig. 2. Peaks at 2969, 2930 and 2868  $\text{cm}^{-1}$  correspond to characteristic C–H stretches on the methyl groups and the peak at 1385  $\text{cm}^{-1}$  is due to a C–H bend on the methyl groups. <sup>1</sup>H-NMR reveals a broad peak centered around 1.5 ppm (relative to TMS) which is indicative of methyl groups.

In preparing the methylated  $C_{60}$ , gentle reflux and 3 h reaction times were necessary because the products of 1 h room temperature reactions were found to still contain some fluorine. A possibility alluded to earlier [8] which is a consequence of the molecule becoming less and less electronegative as successive fluorine atoms are lost [14] may explain the need to apply heat during the reaction for longer periods for complete fluorine removal.

### 3.2. Phenylated $C_{60}$

The phenylated  $C_{60}$  product is brown in color and it is very soluble in toluene and, to a lesser extent, other non-polar, non-aromatic organic solvents. EI mass spectroscopy reveals a range of phenylated  $C_{60}$  species  $C_{60}(\text{C}_6\text{H}_5)_n$  where  $n$  ranges from 1 to 19. The mass spectrum is shown in Fig. 3. The most abundant peak corresponds to  $C_{60}(\text{C}_6\text{H}_5)_{14}$ .

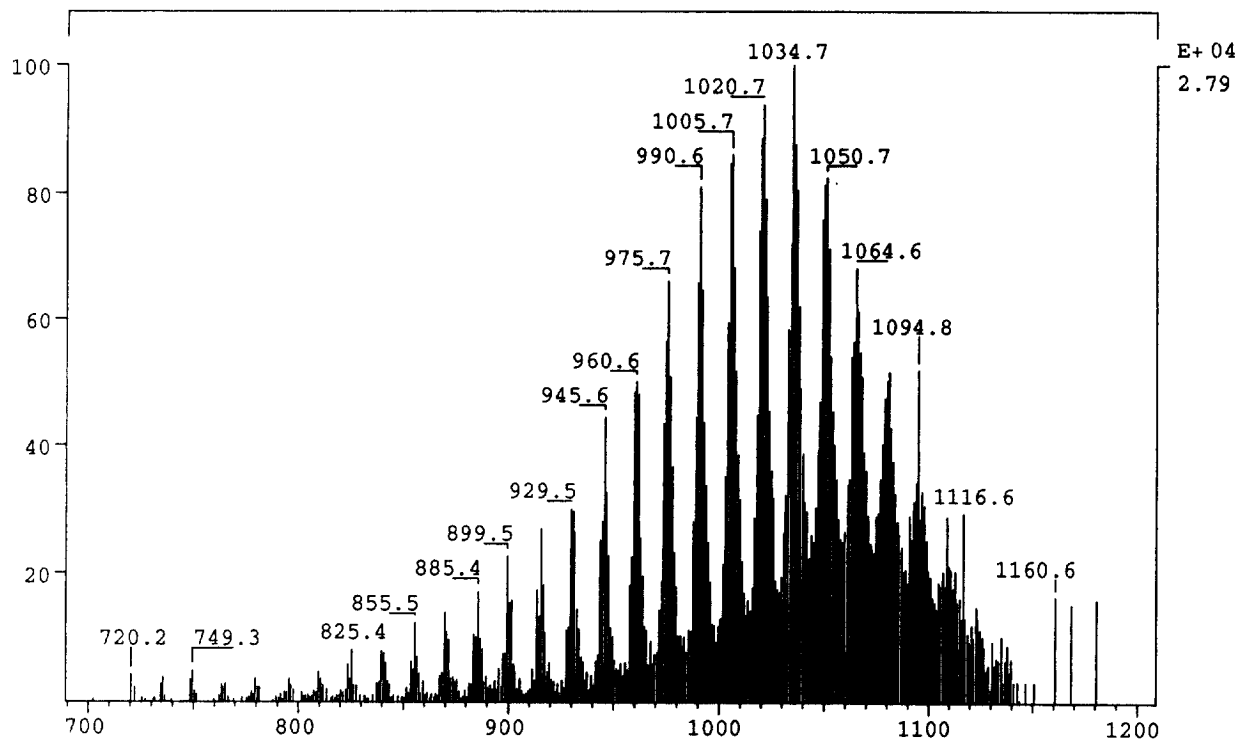


Fig. 1. EI mass spectrum of the methylation product.

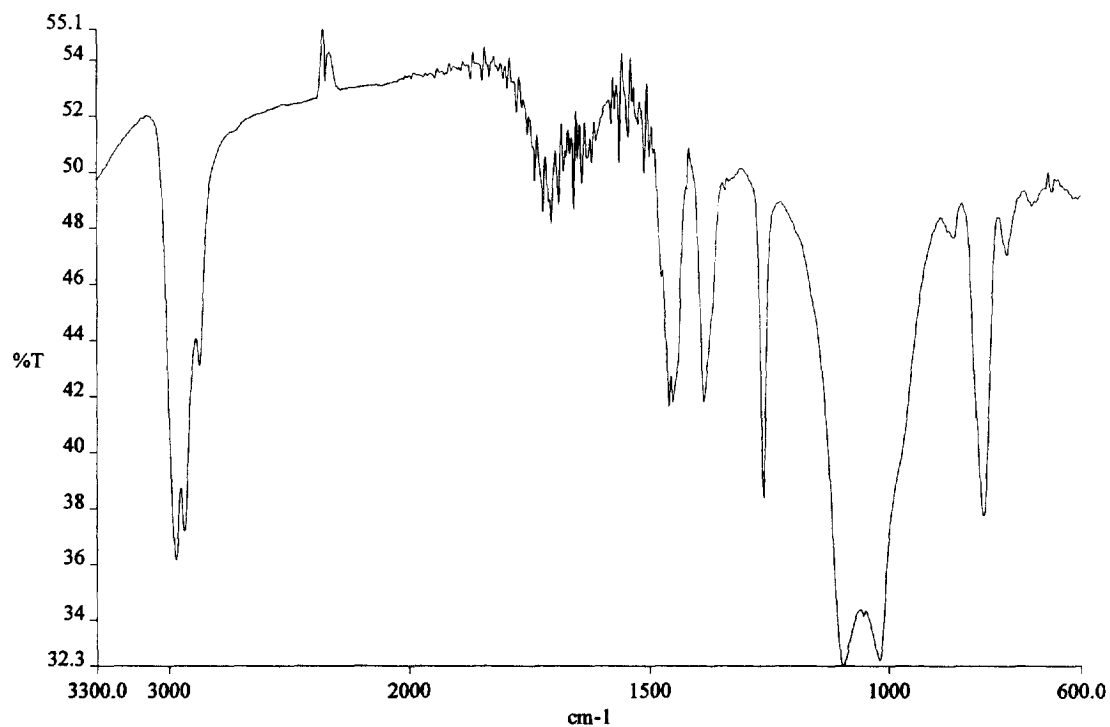


Fig. 2. IR spectrum of the methylation product.

The IR spectrum of the phenylated product can be seen in Fig. 4. The peak at 3050, 2920 and 2850 cm<sup>-1</sup> corresponds to characteristic C–H stretching modes on the phenyl ring while the peaks at 1595, 1490 and 1445 cm<sup>-1</sup>

correspond to C=C stretches of the phenyl rings. Additionally, the <sup>1</sup>H-NMR exhibits a broad peak centered around 7.3 ppm (relative to TMS) which is indicative of phenyl groups.

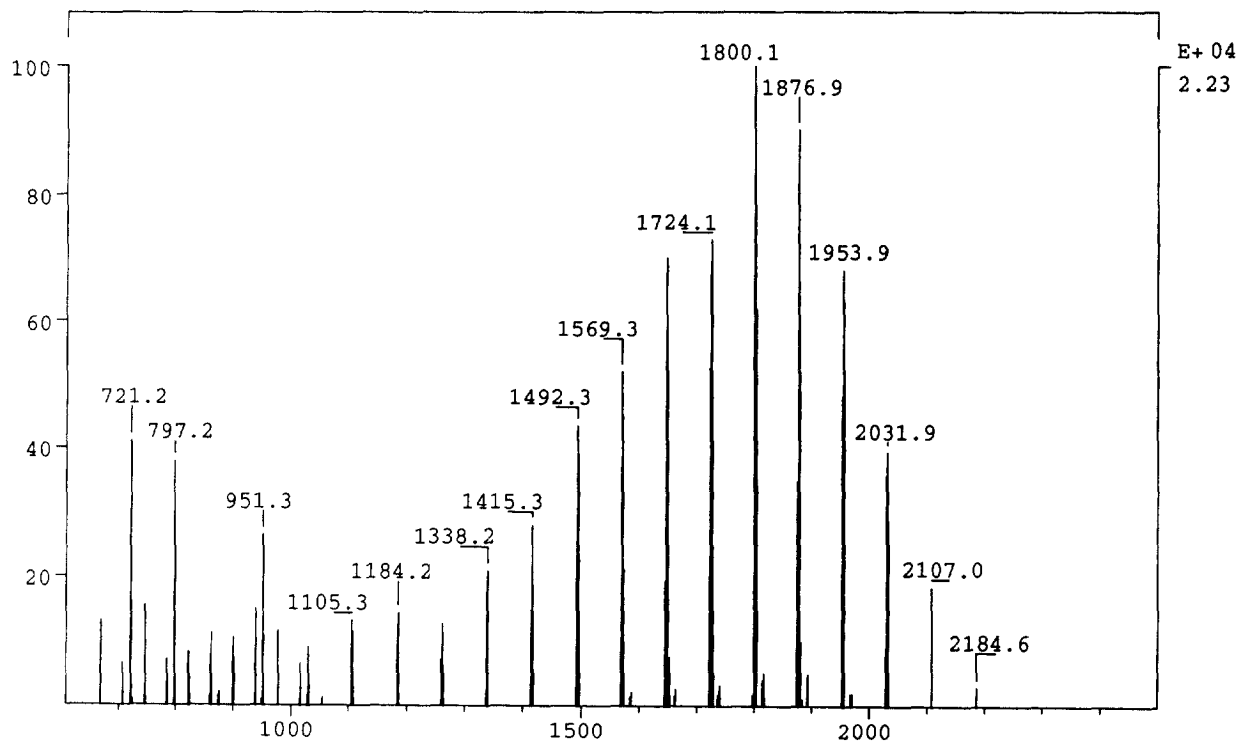


Fig. 3. EI mass spectrum of the phenylation product.

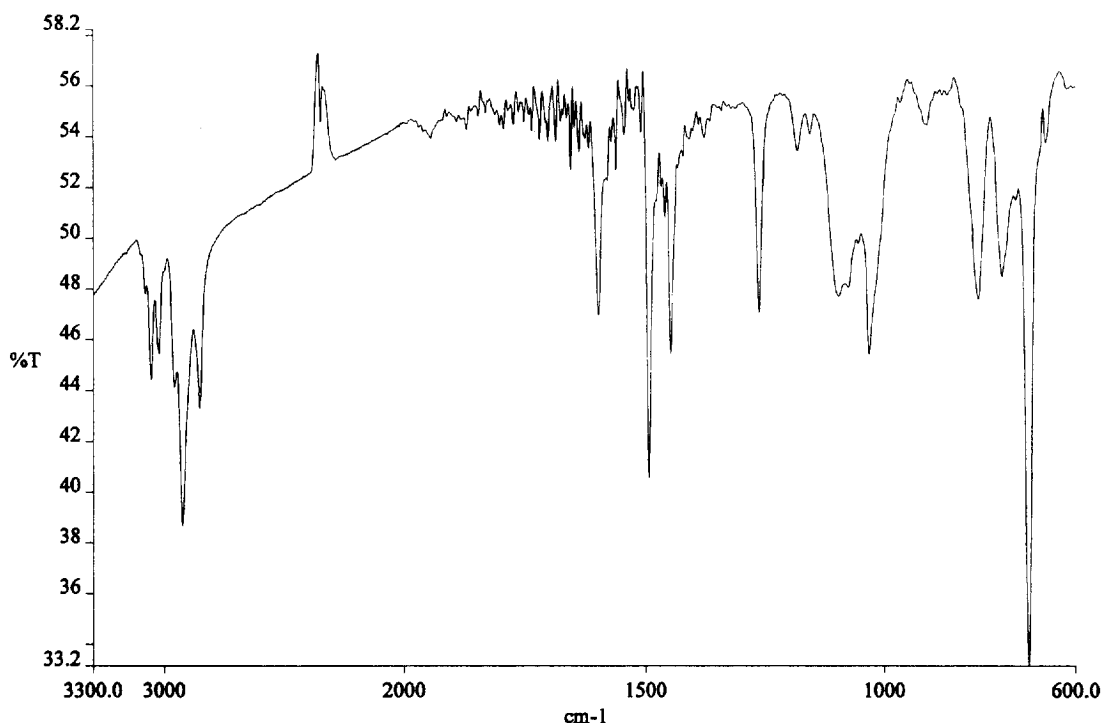


Fig. 4. IR spectrum of the phenylation product.

#### 4. Conclusions

We have fluorinated  $C_{60}$  to yield a  $C_{60}F_{44}$  product and have shown that this product can be reacted with methyl and phenyl lithium reagents to yield methylated and phenylated  $C_{60}$  products. Due to the high reactivity of the fluorinated  $C_{60}$ , we believe that through this process alkylated fullerenes can be synthesized in a relatively straightforward manner giving, perhaps, a higher degree of alkylation than that which is obtained via other synthetic routes.

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