

**Table 2.** Preparation of  $\alpha$ -Methyl  $\beta$ -Substituted  $\beta$ -Fluorovinyl Sulfides **5**

Product	R <sup>1</sup>	T (°C)	Yield (%) <sup>a,b,c</sup>	Z/E <sup>d</sup>
<b>5d</b>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	-78→15	83	60/40
<b>5e</b>	<i>s</i> -C <sub>4</sub> H <sub>9</sub>	-78→15	60	64/36
<b>5f</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	-78→15	NR <sup>e</sup>	—
<b>5g</b>	C <sub>6</sub> H <sub>5</sub>	-78→15	80	66/34
<b>5h</b>	H <sub>2</sub> C=CH	-78→15	53	63/37
<b>5i</b>	C <sub>6</sub> H <sub>13</sub> C≡C	0→15	81	67/33
<b>5j</b>	C <sub>6</sub> H <sub>5</sub> C≡C	0→15	80	68/32

<sup>a</sup>Isolated yield. <sup>b</sup>All products are (E) and (Z) isomeric mixtures. <sup>c</sup>All products were isolated by column chromatography. <sup>d</sup>Ratio was determined by <sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectrum. <sup>e</sup>No reaction.

of **2c** with alkylolithium, vinylolithium, phenyllithium, and lithium alkyl or aryl acetylide at  $-78^{\circ}\text{C}$ , followed by slow warming to ambient temperature, resulted in the formation of corresponding vinyl sulfides **5** in moderate to high yields. However, reaction of **2c** with *t*-BuLi did not occur even at room temperature. The results of these reactions are summarized in Table 2. In particular, compound **2c** can be utilized in the addition-elimination reaction<sup>16</sup> with various types of nitrogen and oxygen nucleophiles which can not be reacted with compound **1c**. Although reactions of **1c** with organolithium compounds except for lithium phenyl acetylide and *t*-BuLi provided the corresponding vinyl sulfides **5**, the use of intermediate **2** in these reactions resulted in the clean formation and easy isolation of **5**.

In a typical procedure, a 250 ml two-neck flask equipped with a septum, a magnetic stir bar and a nitrogen tee connected to a source of argon, was charged with 1,1-bis(phenylthio)-2,2,2-trifluoroethylbenzene (3.76 g, 10.0 mmol) and 50 ml dry THF. The reaction mixture was cooled to  $-78^{\circ}\text{C}$  by using dry-ice/isopropanol slush and phenyllithium (1.8 M solution, 11.2 ml, 20.2 mmol) was added dropwise at  $-78^{\circ}\text{C}$ , followed by slow warming to ambient temperature. The reaction mixture was quenched with water (50 ml) and extracted with ether (50 ml  $\times$  2). After the ether layer was dried with anhydrous MgSO<sub>4</sub>, column chromatography (hexane) provided 2.87 g (94% yield) of 1,2-diphenyl-2-fluorovinyl phenyl sulfide **3g**: m.p.  $53^{\circ}\text{C}$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  7.83-7.50 (m, 5H), 7.41-7.07 (m, 10H); <sup>19</sup>F-NMR (CCl<sub>4</sub>, external standard CF<sub>3</sub>COOH)  $\delta$  -6.67 (s, 1F), -10.57 (s, 1F); IR (KBr) 3050 (w), 1616 (m, C=C), 1577 (m, aromatic C=C), 1473 (m, aromatic C=C), 1438 (m, aromatic C=C), 1215 (m, C-F), 1064 (m), 1022 (m), 929 (m), 736 (s, =C-H OOP), 690 (s, =C-H OOP) cm<sup>-1</sup>; MS, m/e (relative intensity) 306 (M<sup>+</sup>, 100), 196 (43), 185 (25), 121 (32).

**Acknowledgement.** The authors thank the Ministry of Science and Technology and the Maeji Academy Institute at the Yonsei University for financial support, and professor S. K. Choi (KAIST) for recording the <sup>19</sup>F-NMR spectra.

## References

- Presented in part at the 13th International Symposium on Fluorine Chemistry, Bochum, Germany, September 2-6, 1991; For abstract, *J. Fluorine Chem.*, **54**, 123 (1991).
- B. Jiang and Y. Xu, *J. Org. Chem.*, **56**, 7336 (1991) and references cited therein.
- F. Jin, B. Jiang, and Y. Xu, *Tetrahedron Lett.*, **33**, 1221 (1992).
- R. Filler and Y. Kobayashi, *Biomedical Aspects of Fluorine Chemistry*, Kodansha Tokyo, 1982.
- J. T. Welch, *Tetrahedron*, **43**, 3123 (1987).
- J. Mann, *Chem. Soc. Rev.*, **13**, 381 (1987).
- E. Block, "Reactions in Organosulfur Compounds", Academic, New York, 1976.
- B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, **105**, 5075 (1983).
- T. Nakai, K. Tanaka, and N. Ishikawa, *Chem. Lett.*, 1263 (1976).
- A. E. Feiring, *J. Org. Chem.*, **45**, 1962 (1980).
- S. Piettre, Ch. De Cock, R. Merenyi, and H. G. Viehe, *Tetrahedron*, **43**, 4309 (1987).
- T. Fuchigami, Y. Nakagawa, and T. Nonaka, *Tetrahedron Lett.*, **27**, 3869 (1986).
- L. Benati, P. C. Montevicchi, and P. Spagnolo, *J. Chem. Soc. Perkin Trans. I*, 1691 (1990).
- I. H. Jeong, Y. K. Min, Y. S. Kim, K. Y. Cho, and K. J. Kim, *Bull. Korean Chem. Soc.*, **12**, 355 (1991).
- I. H. Jeong, *Bull. Korean Chem. Soc.*, **13**, 468 (1992).
- R. Sauvetre and J. Normant, *Tetrahedron*, **31**, 897 (1975).
- D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, **86**, 883 (1964).
- M. R. Schneider, *J. Med. Chem.*, **29**, 1494 (1986).
- F. Camps, G. Fabrias, and A. Guerrero, *Tetrahedron*, **42**, 3623 (1986).
- S. Eddarir, C. Francesch, H. Mestdagh, and C. Rolando, *Tetrahedron Lett.*, **31**, 4449 (1990).
- Z. Y. Yang and D. J. Burton, *Tetrahedron Lett.*, **31**, 1369 (1990).

## Separation of Fullerene with Poly-p-Phenylene

Sung Ho Kim\*, Jong Shin Yoo<sup>†</sup>, Jee Hyun Hahn<sup>‡</sup>, and Il Cheol Jeon<sup>#</sup>

*Department of Chemistry, Seonam University, Namwon 590-170*

<sup>†</sup>*School of Public Health, Harvard University, Boston, MA 02115, USA*

<sup>‡</sup>*Lab. of Organic Chemistry, OCI Research Center, Incheon 403-020*

<sup>#</sup>*Department of Chemistry, Jeonbuk National University, Jeonju 560-756*

Received November 9, 1992

Because of its various chemical reactivity and applicability,

\*To whom correspondence should be addressed.

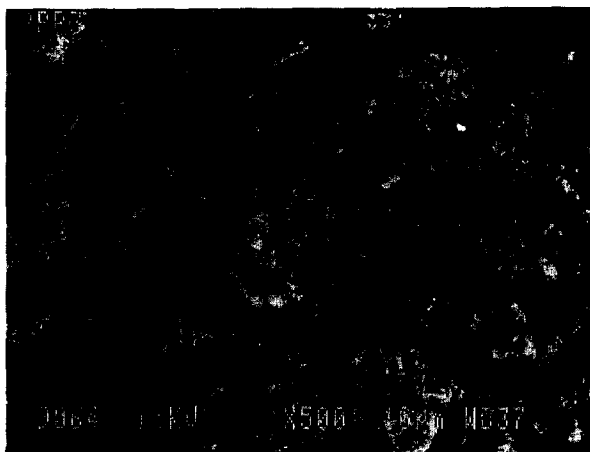


Figure 1. SEM photograph of poly-p-phenylene (PPP).

fullerene, a new form of solid carbon allotropes, has been required for macroscopic quantities in order to satisfy the growing interests of many researchers in this area.<sup>1-4</sup> Fullerene, however, is obtained from the soots in the form of mixture mainly consisting of C<sub>60</sub> and C<sub>70</sub> in toluene extracts. Therefore complete separation of C<sub>60</sub> from C<sub>70</sub> is essential in the fullerene chemistry.

Several separation methods using various chromatographic techniques such as normal/reversed phase and gel permeation columns have already been reported.<sup>5-13</sup> One of the conventional methods in the preparation of pure C<sub>60</sub> and C<sub>70</sub> until now, is to use an alumina/hexane system.<sup>7-11</sup> Because the dissolving power of *n*-hexane for fullerene is so poor to be used in the preparative scale that the separation of C<sub>70</sub> in this system is incomplete, there are lots of efforts to find a chromatographic system utilizing toluene itself as a solvent. One of the promising techniques recently reported is the system utilizing a ground graphite<sup>12</sup> or activated charcoal<sup>13</sup> as the stationary phase. W. A. Scrivens *et al.* developed an activated charcoal-silicagel/toluene system which demonstrated an excellent separation efficiency for C<sub>60</sub>.<sup>13</sup> Even in this method, the separation of C<sub>70</sub> was incomplete and some of the fullerenes were irreversibly adsorbed into the charcoal.

On the other hands, the fullerene compounds have unique geometrical structures. They are consisted of 12 pentagonal faces, but have different number of hexagonal faces; C<sub>60</sub> has 20 six-membered rings while C<sub>70</sub> has 25 six-membered rings. As a result, C<sub>60</sub> is spherical and C<sub>70</sub> is ellipsoidal. As the symmetrical difference due to the number of six-membered rings between C<sub>60</sub> and C<sub>70</sub> could play an important role in their separation, we examine the poly-p-phenylene (PPP) as the stationary phase which is a typical compound with six-membered ring only.<sup>14</sup> Fortunately, since PPP is a fine particle which is insoluble in organic solvent and thermally stable, it can be selected as a packing material for the chromatographic column.<sup>15</sup> Namely, in this communication, in order to obtain the complete separation of C<sub>60</sub> and C<sub>70</sub> in the fullerene mixture, we developed a new liquid chromatographic system with PPP as the stationary phase and pure toluene as the mobile phase respectively.

PPP was prepared from polymerization of benzene according to Kovacic's method<sup>16</sup> and characterized by Fourier trans-

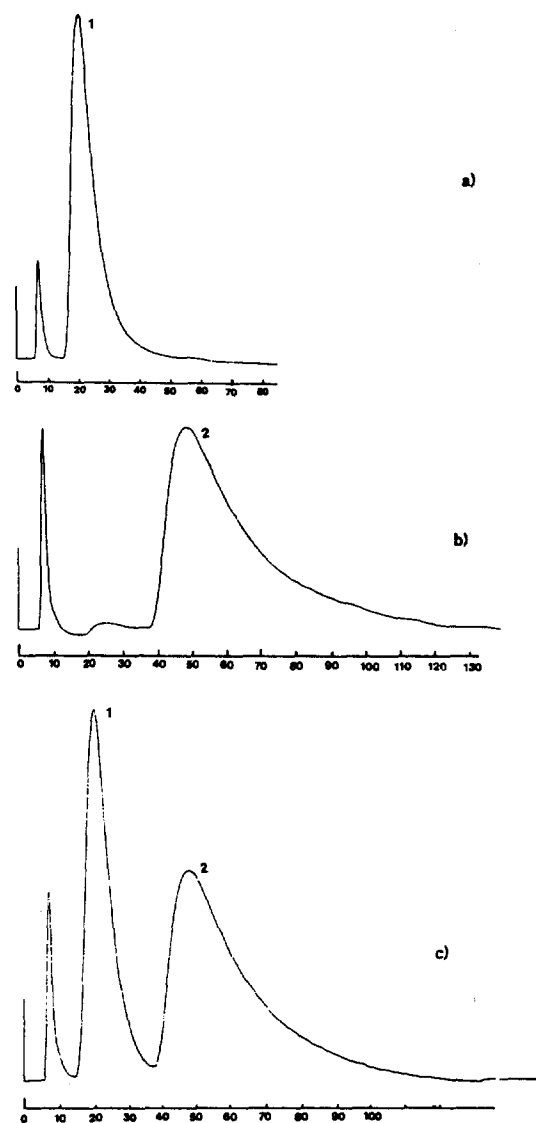


Figure 2. Typical chromatogram of a) standard C<sub>60</sub>; b) standard C<sub>70</sub>; and c) fullerene mixture. (1) C<sub>60</sub>, (2) C<sub>70</sub>

Conditions: PPP as the stationary phase; Toluene as the mobile phase; flowrate 0.7 ml/min; UV detection at 330 nm.

form infrared spectroscopy (FTIR, IFS-48, Bruke Co.), X-ray powder diffractometer (XRD, PW-1710, Philips), and thermal analyzer (TA, TA-9200 system, 951 TGA, 2910 DSC, TA Instruments). It was grounded in the mortar and its size was determined by scanning electron microscope (SEM, JSM-35 CF, JEOL). The column was packed with PPP into a stainless steel tubing (4.6 mm I.D., 30 cm length) under flowing of toluene at 100 psi. A single-piston reciprocating pump (Waters 510, Millipore Co.) was used to deliver toluene as the mobile phase at the flow rate of 0.7 ml/min. Fullerene mixtures were prepared by mixing C<sub>60</sub> ( $2 \times 10^{-4}$  M, 50  $\mu$ l) and C<sub>70</sub> ( $2 \times 10^{-4}$  M, 100  $\mu$ l).<sup>17</sup> Each C<sub>60</sub>, C<sub>70</sub> and mixture was introduced into the column by using a 200  $\mu$ l<sup>18</sup> injection valve (C10U, Valco Instruments). The eluent from the column flowing through a UV-absorbance detector (Waters 486, Millipore, Milford, MA) at the wavelength of 330 nm and the signal was displayed on a chart recorder (Model 585, Linear instru-

ments).

The instrumental data of PPP obtained from FTIR, XRD, and TA are well agreed with those of Kovacic. From the result of SEM showing in Figure 1, the particle diameter of PPP is about 10  $\mu\text{m}$ , but irregularly large particles are observed, too. As PPP particles have weak cohesive property, it is difficult to make their size be uniform. The chromatograms for the separation of  $\text{C}_{60}$  and  $\text{C}_{70}$  in PPP/toluene system are plotted in Figure 2. In Figure 2a, the retention time of air<sup>18</sup> and  $\text{C}_{60}$  at the flow rate of 70 ml/min is 7 and 20 minutes respectively. In Figure 2b, retention time of  $\text{C}_{70}$  is 48 minutes and the impurity peak of  $\text{C}_{60}$ <sup>17</sup> in  $\text{C}_{70}$  is also observed. The resolution capacity factor of  $\text{C}_{70}$  is about 3 times higher than that of  $\text{C}_{60}$ , so the chromatogram of  $\text{C}_{70}$  is much broader than that of  $\text{C}_{60}$ . Figure 2c shows the separation of  $\text{C}_{60}$  from  $\text{C}_{70}$  in its mixture. The retention times of  $\text{C}_{60}$  and  $\text{C}_{70}$  in the mixture are exactly the same as those of individual compound, that is, 20 and 48 min respectively. The complete separation of  $\text{C}_{60}$  and  $\text{C}_{70}$  with the resolution of about 1.5 was achieved. And  $\text{C}_{70}$  is retained over twice longer than  $\text{C}_{60}$ . As mentioned above, it is anticipated that the spherical  $\text{C}_{60}$  seems to elute faster than ellipsoidal  $\text{C}_{70}$  in the present chromatographic condition. It is, however, insufficient to describe the retention mechanism of fullerene in this system. We hope to perform more detailed investigation for the separation mechanism in further study.

Note that our experimental conditions were not optimized for the separation of fullerene in the standard mixture or in the toluene extracts. However the separation ability preliminarily reported here was found to be superior to the existing methods at least by obtaining complete separation of  $\text{C}_{60}$  and  $\text{C}_{70}$  with pure toluene solvent. Clearly, this method could separate larger quantities of raw material from the toluene extracts rapidly using much smaller volume of solvent. Additionally, because the pressure of this system was selected at 100 psi, it is possible to make to pump free system.<sup>19</sup> In the condition of high-pressure packing of PPP, the separation efficiency could be significantly improved.

In conclusion, based on the ideas and data described above, the PPP/toluene system promises a strong possibility that can be used for the separation method of fullerene in toluene extracts. This system can also be extended into a preparatory scale and be an alternative for the conventional activated charcoal/toluene system due to its high separation ability of  $\text{C}_{70}$ .

**Acknowledgement.** The author Sung-Ho Kim thank to Dr. Vernon Reinhold at School of Public Health in Harvard University for his kindness to use of the important instrument set-ups.

## References

- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
- W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature*, **347**, 354-358 (1990).
- P. M. Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Am. Chem. Soc.*, **113**, 2780 (1991).
- I. C. Jeon, S. H. Kim, J. G. Choi, G. H. Lee, S. Y. Hwang, and S. S. Kim, *Bull. Kor. Chem. Soc.*, **13**, 346 (1992).

- R. C. Haddon, L. F. Schneemeyer, J. V. Waszczak, S. H. Glarum, R. Tycko, G. Dabbagh, A. R. Kortan, A. J. Muller, A. M. Mujsce, M. J. Rosseinsky, S. M. Makmhija, F. A. Thiel, K. Raghavachari, E. Cockayne, and V. Elser, *Nature*, **350**, 46 (1991).
- M. S. Meier and J. P. Selegue, *J. Org. Chem.*, **57**, 1924 (1992).
- R. Tayler, J. P. Hare, A. D. Abdul-Sada, and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1423 (1990).
- A. S. Koch, K. C. Khemani, and F. Wudl, *J. Org. Chem.*, **56**, 4543 (1991).
- P. Bhyrappa, A. Penicaud, M. Kawamoto, and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, 936 (1992).
- K. Chatterjee, D. H. Parker, P. Wurz, K. R. Lykke, D. M. Gruen, and L. M. Stock, *J. Org. Chem.*, **57**, 3253 (1992).
- K. C. Khemani, M. Prato, and F. Wudl, *J. Org. Chem.*, **57**, 3254 (1992).
- A. M. Vassallo, A. J. Palmisano, L. S. K. Pang, and M. A. Wilson, *J. Chem. Soc., Chem. Commun.*, 60 (1992).
- W. A. Scrivens, P. V. Bedworth, and J. M. Tour, *J. Am. Chem. Soc.*, **114**, 7917 (1992).
- Of course, graphite and active charcoal are also another example of this type compound.
- As far as we know, The use of PPP as a stationary phase in liquid chromatography has not been reported yet.
- P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).
- The standard solutions were made using conventional separation method of alumina/hexane system. In general, the  $\text{C}_{70}$  solution obtained from this technique, contains about 5% of  $\text{C}_{60}$  as impurities due to incomplete separation of fullerene.
- When the solvents has been used as mobile phase, in order to make the reference peak, the air was injected with sample using the injection valve.
- 100 psi is the obtainable pressure from conventional  $\text{N}_2$  regulator. So ordinary nitrogen tank could substitute the expensive high pressure pump.

## Effect of Fe(II)-Tetradentate Schiff Base Complex on the Electrochemical Reduction of Thionyl Chloride

Woo-Seong Kim, Mee-Suk Shin, Yong-Kook Choi<sup>†</sup>, and Ki-Hyung Chjo

Department of Chemistry, Chonnam University,  
Kwang-Ju 500-757

Received December 21, 1992

The lithium thionyl chloride system has emerged as one of the best primary batteries having combined characteristics of high rate capability, high energy density, long shelf life, and efficient low temperature operation. The electrochemical reduction of thionyl chloride has been studied extensively