

폴리브롬화된 C₆₀의 작용기 변환

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Functional Conversion of Polybrominated Fullerenes

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요 약. 폴리브롬화된 C₆₀의 여러 작용기 변환(방향족화합물과의 프리델-크라프트 플러릴화, 메탁실화, 인산화)이 논의되었다.

ABSTRACT. Functional conversion of polybrominated fullerenes has been discussed. These reactions are Friedel-Crafts fullerylation of aromatics, methoxylation and phosphorylation of polybrominated fullerenes.

INTRODUCTION

A large number of papers have been published about functionalization of fullerenes.¹⁻³ Polychlorination and polybromination of C₆₀ has been done by several groups.⁴ Olah group^(4a) have reported that fullerene reacts with chlorine to afford polychlorinated fullerenes, which undergo their aluminum chloride catalyzed Friedel-Crafts reaction with aromatics to polyarylfullerenes. We now wish to report studies on functionalization of polybrominated C₆₀.

EXPERIMENTAL

Benzene and toluene were distilled before use. Fluorobenzene and aluminum bromide were obtained from Aldrich. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Varian VXR-200 or Unity 300. FAB mass spectra were obtained on a VG2FHF high resolution mass spectrometer. The sample dissolved in chloroform was deposited on nitrobenzyl alcohol as the matrix. High energy xenon atoms were used for bombardment.

Fullerylated benzene. C₆₀ (25 mg, 0.035 mmol)

was reacted with excess bromine (4 mL, 78 mmol), overnight, to give C₆₀Br₂₄, which remain on the flask after unreacted bromine was evaporated under N₂ atmosphere. Stirring a benzene solution (20 mL, 0.22 mol) of C₆₀Br₂₄ with aluminum bromide (30 mg, 0.11 mmol) at ambient temperature for 4 hours gave a dark reddish-brown solution which upon aqueous work-up gave a brown solid (soluble in chloroform). ¹H NMR (CDCl₃) δ 7.25(br s). ¹³C NMR (CDCl₃) δ 128(br s).

Similar conditions were used for the reaction of C₆₀Br₂₄ with toluene and fluorobenzene. The products gave the following characteristics.

Fullerylated toluene. ¹H NMR (CDCl₃) δ 2.2(br s), 6.8(br s). ¹³C NMR (CDCl₃) δ 20.9(br s), 128.2(br s), 135.9(br s).

Fullerylated fluorobenzene. ¹H NMR (CDCl₃) δ 7.0(br s). ¹³C NMR (CDCl₃) δ 115.1(br s), 129.5(br s). ¹⁹F NMR (CDCl₃, internal standard CFCl₃) δ -114.1(several broad peaks).

Polymethoxylated fullerenes from C₆₀Br₆. The polybrominated fullerene (C₆₀Br₆, 20 mg, 0.02 mmol) was treated with excess methanol/KOH at 60 °C for 2 days. After following aqueous work-up, it

was extracted with chloroform. The solvent was evaporated to give a yellowish material. ^1H NMR (CDCl_3) δ 3.8(br s). ^{13}C NMR (CDCl_3) δ 55.6(br s), 148.7(br s).

Polymethoxylated fullerenes from $\text{C}_{60}\text{Br}_{24}$. ^1H NMR (CDCl_3) δ 3.6(br s). ^{13}C NMR (CDCl_3) δ 54.9(br s), 144(br s).

Polyphosphorylation of $\text{C}_{60}\text{Br}_{24}$. A suspension of $\text{C}_{60}\text{Br}_{24}$ (16 mg, 0.006 mmol) in tetrahydrofuran (10 mL) (which was prepared from C_{60} (5 mg, 0.007 mmol) with Br_2 (2 mL, 39 mmol)) was added a solution of $(\text{EtO})_2\text{POLi}$ (0.14 g, 1 mmol) in tetrahydrofuran (10 mL) at 0°C . $(\text{EtO})_2\text{POLi}$ was generated from $(\text{EtO})_2\text{POH}$ (0.13 mL, 1 mmol) with BuLi (0.4 mL, 2.5 M solution in hexane) at -78°C . The reaction mixture turned into a clear dark-solution immediately. The reaction mixture was stirred at room temperature for 0.5 hour. After solvents were removed, the residue was quenched with water, filtered and washed with water several times. The obtained brown powder was dried in an oven at 110°C and was shown to be a mixture of $\text{C}_{60}[\text{PO}(\text{OEt})_2]_n$. ^1H NMR (CDCl_3) δ 1.4(br s), 4.4(br s). ^{13}C NMR (CDCl_3) δ 16.7(br s), 64.9(br s), 147.9(br s).

RESULTS AND DISCUSSION

Friedel-Crafts fullerylation of aromatics. Polybrominated fullerene ($\text{C}_{60}\text{Br}_{24}$) undergoes Friedel-Crafts type fullerylation of aromatics (benzenes, toluene and fluorobenzene) catalyzed by aluminum

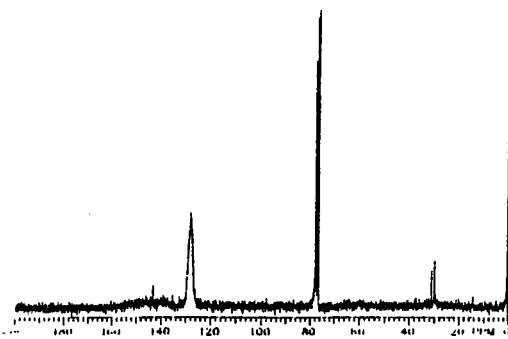
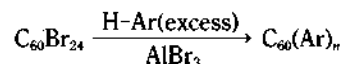


Fig. 1. 50 MHz ^{13}C NMR spectrum of fullerylated benzenes.

bromide.^{4(a)} The ^1H NMR spectrum showed a broad absorption centered at δ 7.25 ppm. The ^{13}C NMR spectrum (Fig. 1) also showed a broad absorption at δ 128 ppm indicating phenylation.



The FAB mass spectrum indicates substitution of at least 16 phenyl groups (M^+ , 1995), which is different from the number of phenyl substitution of polychlorinated fullerenes.⁵ Consecutive loss of phenyl groups, demonstrating the fragmentation from $\text{C}_{60}(\text{C}_6\text{H}_5)_{16}$ to $\text{C}_{60}(\text{C}_6\text{H}_5)_n$, has also been observed. In addition to phenyl substitution, benzene addition (i.e., C_6H_6 and H) was also observed. ^1H NMR spectrum of fullerylated toluene showed broad absorptions centered at δ 2.2 and 6.8 ppm. The ^{13}C NMR spectrum also showed broad absorptions at δ 20.9, 128.2 and 135.9 ppm. The FAB mass spectrum indicates substitution of at least 16 tolyl groups (M^+ , 2184). ^{13}C NMR spectrum of fullerylated fluorobenzene showed a broad absorption centered at δ 115.1 and 129.5 ppm. ^{19}F NMR spectrum showed several broad peaks around δ -114.1 ppm. The FAB mass spectrum indicates substitution of at least 15 fluorophenyl groups (M^+ , 2148).

Methoxylation of polybrominated fullerenes. Polybrominated fullerenes (C_{60}Br_6 or $\text{C}_{60}\text{Br}_{24}$) were treated with excess methanol/KOH at 60°C for 2 days to afford polymethoxylated fullerenes. The ^1H NMR spectrum of the product obtained from C_{60}Br_6 indicated a broad envelope of methoxy groups centered at δ 3.8 ppm. The ^{13}C NMR spectrum also showed two broad absorptions at δ 55.6 and 148.7 ppm. The evidence for the substitution of the bromine atoms by methoxy groups came from FAB mass spectrometry (polymethoxylation up to 26 methoxy group, M^+ , 1536). Sequential loss of methoxy groups was observed, indicating fragmentation from $\text{C}_{60}(\text{OMe})_{26}$ all the way to $\text{C}_{60}(\text{OMe})$. Observation of a product component with 26 methoxy groups implies that more than 6 bromine atoms may have added to the fullerene skeleton. The reaction may go through an unprece-

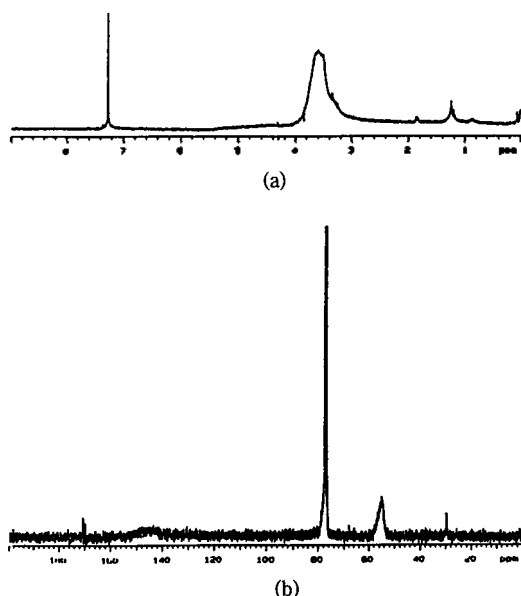
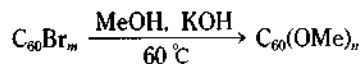


Fig. 2. (a) 300 MHz ¹H NMR spectrum of polymethoxylated fullerenes. (b) 50 MHz ¹³C NMR spectrum of polymethoxylated fullerenes.

dented frontside nucleophilic substitution process.



¹H NMR spectrum (Fig. 2(a)) of polymethoxylated fullerenes (obtained from C₆₀Br₂₄) showed a broad absorption at δ 3.6 ppm. ¹³C NMR spectrum (Fig. 2 (b)) showed broad absorptions at δ 54.9 and 144 ppm. The FAB mass spectrum indicated many ion fragments, but two main distributions m/z: 450~700 and 1300~1500 due to hydroxylated products.

Phosphorylation of polybrominated fullerenes.

A suspension of C₆₀Br₂₄ (or C₆₀Br₆) in tetrahydrofuran was added to a solution of (EtO)₂POLi in tetrahydrofuran at 0 °C to furnish a mixture of C₆₀[PO(OEt)₂]_n. The ¹H NMR spectrum (Fig. 3(a)) showed two broad peaks at δ 1.4 and 4.4 ppm. Integration of the peaks showed about 2 : 3 relative intensity. The ¹³C NMR spectrum (Fig. 3(b)) showed broad peaks at δ 16.7, 64.9 and 147.9 ppm. FAB mass spectrometry of the product of C₆₀Br₆ and (EtO)₂POLi indicated poly(diethyl)phosphorylation with 3 to 5 (diethyl)phosphoryl groups (M⁺, 1393).

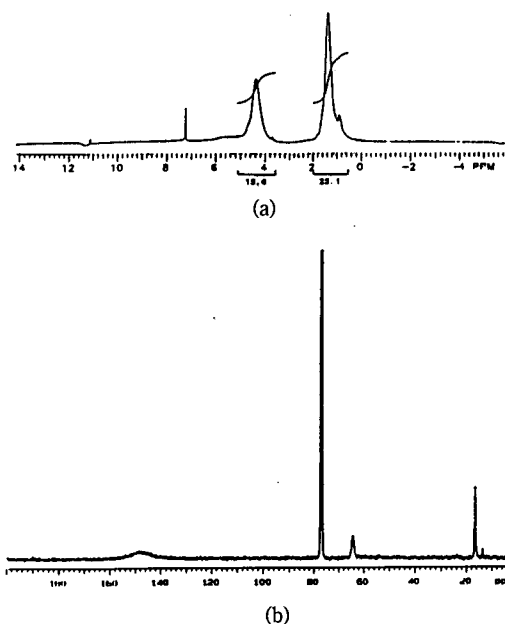
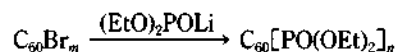


Fig. 3. (a) 200 MHz ¹H NMR spectrum of poly(diethyl)-phosphorylated fullerenes. (b) 75 MHz ¹³C NMR spectrum of poly(diethyl)-phosphorylated fullerenes.



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