J. Org. Chem. **1996,** *61,* 8500−8502

Synthesis of Disubstituted 1,2-Dihydro[60]fullerenes with Well-Defined Structure by Addition of 1-Alkoxy-1-chloroethanes to 2-(1-Octynyl)-1,2-dihydro[60]fulleren-1-ide Ion

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Received July 12, 1996[⊗]

We report the preparation of disubstituted 1,2-dihydro[60]fullerenes having functional groups, namely 1-(1-octynyl)-2-(1-isobutoxyethyl)-1,2-dihydro[60]fullerene and 1-(1-octynyl)-2-[1-(2-acetoxyethoxy)ethyl]-1,2-dihydro[60]fullerene, by coupling 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion with carbon electrophiles derived from vinyl ethers. The structure and redox properties of the products were examined by ^{1}H and ^{13}C NMR spectra and cyclic voltammetry.

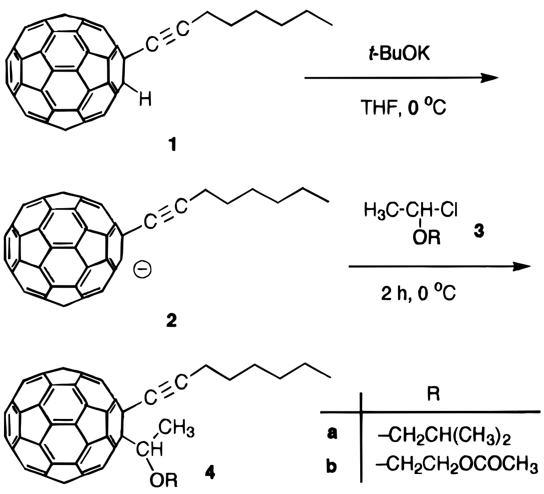
Introduction

Low solubility and poor processability are two major disadvantages of [60]fullerene in the application to advanced materials. In order to overcome these disadvantages, various chemical modifications of fullerene have been extensively studied.[1] However, only a few studies have been reported on the disubstituted derivatives of 1,2-dihydro[60]fullerene with well-defined structure.[2−5] Such derivatives are advantageous in that not only the solubility is improved but also two different functional groups could be incorporated.

Recently, Murata et al. have succeeded in preparing a stable carbanion of a C_{60} derivative with the well-defined structure, i.e. 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion.[3] The precursor of this anion can be synthesized in high yield, and the anion can be generated quantitatively. It was expected to obtain C_{60} derivatives having two organic addends, especially those with functional groups, by addition of electrophilic species having a functional group to this carbanion.

In this note, we report the preparation of such disubstituted 1,2-dihydro[60]fullerenes having functional groups by coupling 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion with carbon electrophiles derived from vinyl ethers. The structure and redox properties of the products were examined by ^{1}H and ^{13}C NMR spectra and cyclic voltammetry.

Scheme 1



Results and Discussion

Synthesis of Disubstituted Derivatives of 1,2-Dihydro[60]fullerene. Disubstituted derivatives of 1,2-dihydro[60]fullerene, **4a** and **4b**, were prepared by addition of carbon electrophiles **3**, derived from vinyl ethers, to 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion as shown in Scheme 1. 2-(1-Octynyl)-1,2-dihydro[60]fulleren-1-ide ion (**2**) was generated by deprotonation of 1-(1-octynyl)-1,2-dihydro[60]fullerene prepared according to the method of Murata et al.[3] The electrophiles **3** were prepared by bubbling HCl gas into the hexane solution of corresponding vinyl ether (VE), i.e. isobutyl vinyl ether (IBVE) and 2-acetoxyethyl vinyl ether (AcOVE) at 0 °C.[6,7] To a dark green solution of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion **2** in THF was slowly added 6 equiv of a hexane solution of VE-HCl adduct **3** with vigorous stirring. After the reaction of 2 h, the resulting brownish solution was quenched with methanol and subjected to the chromatographic separation using hexane as eluent. The products **4a** and **4b** were obtained as dark brown powders in 39% and 54% yield, respectively. The addition of the electrophile having a more polar substituent seems to give the

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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S0022-3263(96)01320-5 CCC: $12.00

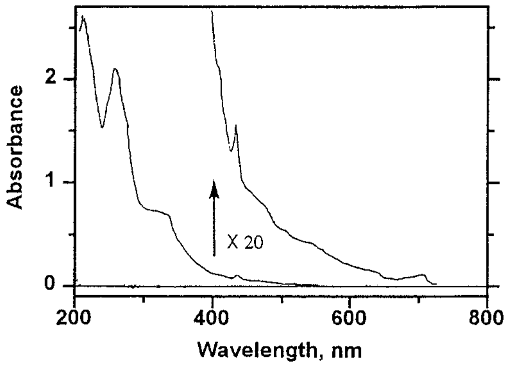


Figure 1. UV-vis spectrum of disubstituted C_{60} derivative **4a** in cyclohexane (2.04×10^{-5} M). Compound **4b** showed a similar spectrum.

product in a higher yield. The starting material **1** was recovered in 31% and 18%, respectively. The C_{60} derivatives with two organic addends, **4a** and **4b**, are soluble not only in nonpolar organic solvents such as toluene, $CHCl_3$ and CS_2, but also in polar organic solvents such as THF in a considerably high concentration of at least 34 mg of **4b**/mL as an example. Thus, the structural modification in the present study was found to be an effective means for improvement on solubility of the [60]fullerene derivatives.

Structural Identification. In previous studies, the positional selectivity in the addition of the electrophile to C_{60} carbanion having an organic addend was shown to be highly dependent on the organic group already present on the C_{60} core. In the case of 2-*tert*-butyl-1,2-dihydro[60]fulleren-1-ide ion, a stable carbocation such as the tropylium ion was found to add at the 4-position.[5] In contrast, in the case of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion, simple alkyl groups such as methyl and ethyl groups add at the 2-position, while tropylium ion adds at both the 2- and 4-positions and benzoyl group adds selectively at the 4-position.[3] Thus, it is of considerable interest to examine which mode of addition would occur for the present electrophiles.

As shown in Figure 1, the UV-vis spectra of both **4a** and **4b** exhibited an absorption pattern with a sharp absorption at around 430 nm, which is diagnostic of the C_{60} derivative with two organic groups attached at the 1,2-positions of the 6,6-juncture bond.

The ^1H NMR data demonstrated that both the product **4a** and **4b** are a single isomer (see Experimental Section). The methine and methyl protons of the 1-isobutoxyethyl group of **4a** exhibited a marked downfield shift for the alkoxyethyl group (δ 5.72 and 2.27, respectively) as compared with those of 1-isobutoxyethyl chloride, i.e. IBVE-HCl adduct **3a** (δ 5.69 and 1.70, respectively). This is attributed to the deshielding effect of the C_{60} core[8] and also to the triple bond attached in close proximity.

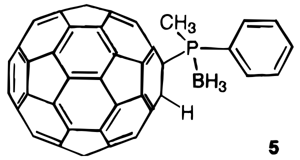
The ^{13}C NMR spectrum exhibited signals for one pair of acetylenic carbons (δ 85.71, 80.52), sp^3 carbons in the C_{60} core (δ 71.32, 59.02), and sp^3 carbons in the octynyl and alkoxy groups, and, most importantly, partly overlapped 58 signals for the sp^2 carbons of the C_{60} core. The similar general features were also observed in the ^1H and ^{13}C NMR spectra of **4b**.

The most C_{60} derivatives so far reported to have two different organic groups at the 1,2-positions of the 6,6-juncture bond, have a C_s symmetry with the plane of symmetry bisecting the C_{60} core along the 6,6-bond. In contrast, the 1,2-bisadducts, **4a** and **4b**, of the present study do not have the C_s symmetry due to the asymmetric carbon of the 1-alkoxyethyl group directly attached to the C_{60} core and therefore exhibit nearly 60 signals for the sp^2 carbons of the C_{60} core. The similar phenomenon is observed in the case of the C_{60} derivative having a chiral phosphine−borane moiety such as in **5**.[9] Thus, from all the spectral data, the products in the present study are concluded to have the two organic groups at the 1,2-positions of the 6,6-juncture bond.

Table 1. Results of Cyclic Voltammetry[a]

compd	E_{ox} irrev peak potl	reversible, $E_{1/2}$ $E_{red}{}^1$	$E_{red}{}^2$	$E_{red}{}^3$
C_{60}	+1.41	−0.93	−1.36	−1.85
4a	+1.43	−1.05	−1.48	−2.05
4b	+1.44	−1.04	−1.46	−2.01

[a] Potential in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 M) as a supporting electrolyte; scan rate, 0.1 V s^{-1}.



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The redox properties of the newly obtained **4a** and **4b** were examined by the use of cyclic voltammetry in benzonitrile. The voltammograms exhibited a single irreversible oxidation peak and three reversible reduction waves as in the case of C_{60}. The results are shown in Table 1. The reduction potentials of **4a** and **4b** were more negative by slightly more than 0.1 V as have been commonly observed for the disubstituted 1,2-dihydro[60]fullerenes.[10]

It is of interest to note that the alkyl chlorides, the reactivity of which is generally lower than bromides or iodides, smoothly reacted with anion **2**. The presence of the alkoxy group, which has the strong ability to polarize the C−Cl bond, must be responsible to this high reactivity. The present results clearly demonstrated that the VE-HCl adducts can react with the carbanion of a C_{60} derivative to give a 1,2-bisadduct with a well-defined structure. It is expected that the present work can be applied for preparation of C_{60}-capped polymer of vinyl ether by the use of reaction of living end of cationic polymerization with organo-C_{60} carbanion. The study is now underway to explore this possibility.

Experimental Section

Measurements. NMR spectra were observed at 400 MHz for ^1H and 75 and 67.5 MHz for ^{13}C NMR. Cyclic voltammetry was conducted using a three-electrode cell with a glassy carbon working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potential was read with respect to ferrocene added as an internal standard.

Materials. C_{60} was separated from a commercial C_{60}/C_{70} mixture (ca. 80:20 by weight; Term Co.) by the use of a Norit

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carbon−silica gel column eluted with toluene. THF was freshly distilled from sodium benzophenone ketyl before use. AcOVE was prepared as reported previously.[6] Hexane, IBVE, and AcOVE were distilled from CaH_2. Benzonitrile was distilled from P_2O_5. Reactions were conducted under nitrogen atmosphere in predried glassware. 1-(1-Octynyl)-1,2-dihydro-[60]fullerene (**1**) was prepared according to the literature method.[3] The IBVE-HCl adduct (**3a**) and AcOVE-HCl adduct (**3b**) were prepared by bubbling HCl gas to the corresponding IBVE hexane solutions of vinyl ethers in hexane.[6,7]

1-(1-Octynyl)-2-(1-isobutoxyethyl)-1,2-dihydro[60]-fullerene (4a). A solution of 2-(1-octynyl)-1,2-dihydro[60]-fulleren-1-ide ion (**2**) was prepared by adding 0.16 mL (0.0144 mmol) of 0.0881 N *t*-BuOK in THF to a stirred solution of **1** (12.33 mg, 0.0144 mmol) in 20 mL of THF at room temperature and stirring the mixture for 15 min at 0 °C.[3] To a vigorously stirred solution of **2** was added a 1.4 N solution of **3a** in hexane (0.06 mL, 0.084 mmol) dropwise over 2 min. After the reaction of 2 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluting with hexane. From the first fraction was obtained unreacted **1** (3.44 mg, 31%). From the second fraction was isolated the product **4a** (4.33 mg, 39%) as a dark brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (q, 1H), 3.80 (m, 1H), 3.69 (m, 1H), 2.60 (t, 2H), 2.27 (d, 3H), 2.07 (m, 1H), 1.83 (quint, 2H), 1.61 (quint, 2H), 1.41 (m, 6H), 1.04 (d, 6H), 0.94 (t, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 155.16, 154.44, 154.18, 152.74, 148.04, 147.85, 147.82, 147.68, 147.59, 146.47, 146.41, 146.27, 146.24, 146.20, 146.19, 149.14, 146.01, 145.92, 145.45, 145.43, 145.39, 145.31, 145.28, 145.26, 145.14, 145.04, 144.79, 144.68, 144.66, 144.57, 143.10, 143.09, 143.06, 142.60, 142.57, 142.34, 142.20, 142.14, 142.13, 142.06, 141.89, 141.63, 141.61, 141.46, 141.33, 141.18, 140.32, 140.20, 139.27, 138.78, 135.71, 135.22, 134.08, 134.01 (54 signals, sp^2-carbons in the C_{60} core), 85.71 ($C\equiv C$), 80.52 (CHO), 80.44 ($C\equiv C$), 76.76 (CH_2O), 71.32, 59.02 (quaternary sp^3-C in the C_{60} core), 31.43, 29.70 (CH_2), 29.18 (CH), 28.96, 22.67 (CH_2), 20.54, 19.77 (CH_3 in IBVE), 19.65 (CH_2), 14.12 (CH_3); UV-vis (cyclohexane) λ_{max} 213 nm (log ϵ 5.13), 256 (5.08), 328 (4.58), 432 (3.61), 702 (2.68); MS (DCI$^-$) *m*/z 930, (M$^-$), 720, (C_{60}^-).

1-(1-Octynyl)-2-[1-(2-acetoxyethoxy)ethyl]-1,2-dihydro-[60]fullerene (4b). Similarly, a solution of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion (**2**) was prepared by adding 0.63 mL (0.046 mmol) of 0.0725 N *t*-BuOK in THF to a stirred solution of **1** (38.11 mg, 0.046 mmol) in 40 mL of THF at room temperature and stirring for 15 min at 0 °C. To a vigorously stirred solution of **2** was added a 0.70 N solution of **3b** in hexane (0.4 mL, 0.28 mmol) dropwise over 2 min. After 2 h, the brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluting with hexane. From the first fraction was obtained unreacted **1** (7.90 mg, 18%). From the second fraction was isolated the product **6** (23.70 mg, 54%) as dark brown solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.80 (q, 1H), 4.39 (m, 2H), 4.20 (m, 2H), 2.62 (t, 2H), 2.29 (d, 3H), 2.04 (s, 3H), 1.82 (quint, 2H), 1.61 (quint, 2H), 1.41 (m, 6H), 0.94 (t, 3H); ^{13}C NMR(75 MHz, CD_2Cl_2) δ 170,41 (CO) ,154.87, 154.12, 153.36, 152.15, 147.72, 147.71, 147.52, 147.40, 147.28, 146.18, 146.17, 145.96, 145.92, 145.90, 145.85, 145.71, 145.62, 145.10, 145.09, 145.05, 144.95, 144.93, 144.72, 144.64, 144.45, 144.37, 144.28, 144.19, 142.80, 142.74, 142.31, 142.29, 142.03, 141.84, 141.79, 141.52, 141.43, 141.31, 141.28, 141.19, 141.04, 140.91, 140.01, 139.91, 139.86, 138.91, 138.55, 135.52, 135.18, 133.73, 133.67 (51 signals, sp^2-carbons in the C_{60} core), 85.93 ($C\equiv C$), 80.92 (CHO), 79.83 ($C\equiv C$), 70.87 (quaternary sp^3-C in the C_{60} core), 68.04, 63.31 (CH_2O), 58.70 (quaternary sp^3-C in the C_{60} core), 31.38, 28.61 (CH_2), 28.46 (CH_3-CO), 28.37, 22.33 (CH_2), 20.30 (CH_3 in AcOVE), 19.17 (CH_2), 13.54 (CH_3); UV-vis (cyclohexane) λ_{max} 213 nm (log ϵ 5.13), 255 (5.08), 328 (4.58), 432 (3.61), 701 (2.68); MS (DCI$^-$) *m/z* 829, (M$^-$ − AcOVE), 720, (C_{60}^-).

Supporting Information Available: The ^{1}H NMR, ^{13}C NMR, and UV-vis spectra of **4a** and **4b**, cyclic voltammograms of **4a** and **4b**, mass spectrum of **4a** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961320X