ORGANIC LETTERS

2004
Vol. 6, No. 16
2797−2799

Synthesis of [60]Fullerene Adducts Bearing Carbazole Moieties by Bingel Reaction and Their Properties

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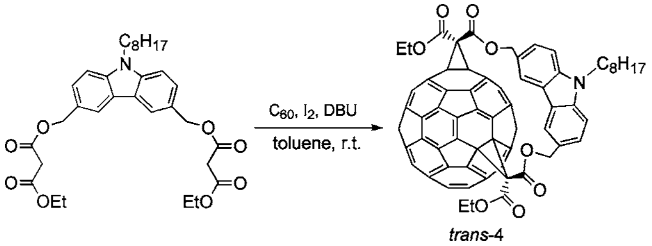
Received June 5, 2004

ABSTRACT



Carbazole-linked [60]fullerene adducts were successfully prepared by the Bingel reactions using carbazole derivatives bearing one or two ethyl malonate moieties. In the latter cases, specific bisadduct regioisomers were obtained, depending on the spacer unit between two ethyl malonate moieties.

The photoconductivity of poly(*N*-vinylcarbazole) (PVCz) doped with electron acceptors such as fullerenes has attracted much attention.[1] In this context, the photoinduced electron transfer between fullerenes and PVCz or related compounds in solution or films has been intensively investigated.[2] In contrast, there have been limited examples of fullerene adducts bearing carbazole moieties linked by covalent bondings and investigation on their intramolecular electron and/or energy transfer, although such compounds are suitable for the analysis of the relationship between the arrangement of two chromophores and the photophysical behavior. While some carbazole-linked fullerene adducts (fulleropyrrolidines) prepared by Prato reaction are known in the literature,[3,4] no carbazole-linked fullerene adducts prepared by Bingel reaction have so far been reported, despite its versatility for fullerene functionalization.[5] This is probably because the precursor malonate esters and resulting fullerene adducts are rather labile under certain conditions as described below. Herein, we report the first successful synthesis and isolation of carbazole-linked [60]fullerene mono- and bisadducts by the Bingel reactions using precursors **1**−**3**.

Precursors **1**−**3** were prepared by $NaBH_4$ reduction of the corresponding mono- or dialdehydes **10**−**12**, followed by the reaction of ethyl 3-chloro-3-oxopropionate in the presence of pyridine, as shown in Scheme 1. Dialdehyde **12** was prepared by the treatment of 1,5-bis(*N*-carbazolyl)-3-oxapentane with $POCl_3$ and DMF in refluxed 1,2-dichloroethane, in a manner similar to **11**.[6] Since **1**−**3** were found to gradually decompose on silica gel column chromatography, they were purified by using aluminum oxide and successfully isolated.

The Bingel reaction of **1** with [60]fullerene was carried out under conventional conditions:[7] **1** was allowed to react

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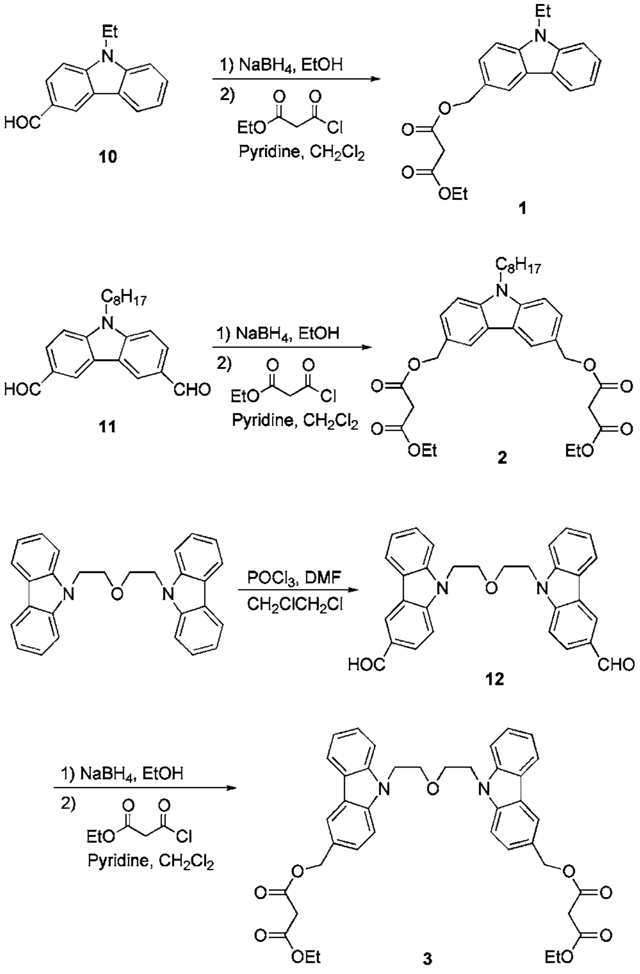
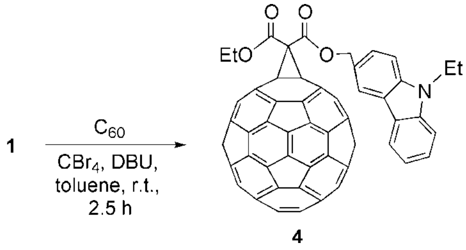
10.1021/ol048952n CCC: $27.50 © 2004 American Chemical Society
Published on Web 07/03/2004

Scheme 1. Preparation of **1**−**3**



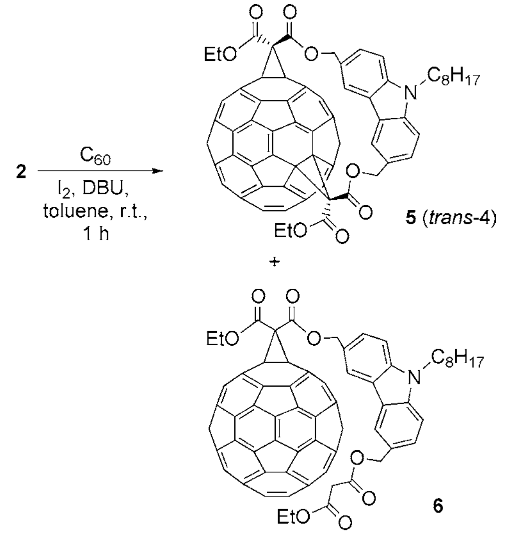
with [60]fullerene, CBr_4, and DBU in toluene at room temperature for 2.5 h to give monoadduct **4** in 22% isolated yield (Scheme 2). Monoadduct **4**, which is unstable against silica gel similar to **1**, was isolated by column chromatography (aluminum oxide) with toluene as the eluent. The ^{1}H NMR spectrum of **4** is consistent with its structure: seven aromatic proton peaks, *N*- and *O*-ethyl proton peaks, and a benzyl proton peak (singlet) are observed.[8]

Scheme 2. Bingel Reactions Using **1**



The Bingel reaction using bis(malonate) **2** afforded bisadduct **5** in 19% yield (based on the consumed [60]fullerene (61%)) as a single regioisomer, along with monoadduct **6** and a recovery of unreacted [60]fullerene (Scheme 3). In this case, the use of I_2 instead of CBr_4 increased the yields of products. It is noteworthy that **5** was selectively produced among eight possible regioisomers. The ^{1}H NMR spectrum of **5** exhibited three aromatic proton peaks, one set of ethyl

Scheme 3. Bingel Reactions Using **2**



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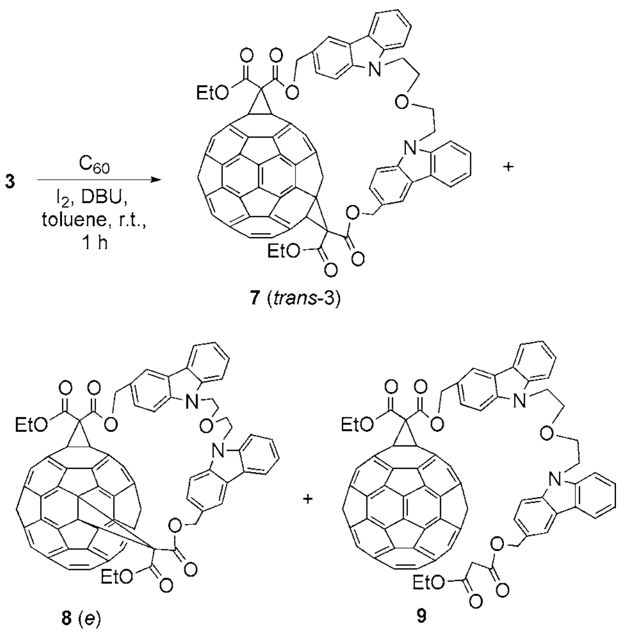
(8) Selected spectroscopic data of monoadduct **4** and bisadducts **5** and **7**. **4**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.24 (1H, s), 8.07 (1H, d, $J = 7.6$ Hz), 7.61 (1H, d, $J = 8.2$ Hz), 7.47 (1H, t, $J = 7.3$ Hz), 7.39 (2H, m), 7.23 (1H, t, $J = 7.3$ Hz), 5.72 (2H, s), 4.46 (2H, q, $J = 7.0$ Hz), 4.35 (2H, q, $J = 7.3$ Hz), 1.42 (3H, t, $J = 7.3$ Hz), 1.33 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 163.54, 145.24, 145.17, 145.06, 144.99, 144.94, 144.78, 144.65, 144.58, 144.53, 144.31, 144.19, 143.81, 143.67, 142.98, 142.90, 142.89, 142.69, 142.13, 141.80, 141.68, 140.83, 140.73, 140.33, 140.24, 139.47, 138.40, 127.57, 126.07, 125.19, 123.14, 122.75, 122.41, 120.66, 119.18, 108.60, 108.47, 71.58, 70.05, 63.41, 52.25, 37.67, 14.08, 13.89; APCI MS *m/z* 1057 (M$^-$). **5**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.10 (2H, s), 7.51 (2H, d, $J = 8.2$ Hz), 7.24 (2H, d, $J = 8.2$ Hz), 5.75 (2H, d, $J = 11.3$ Hz), 5.66 (2H, d, $J = 11.3$ Hz), 4.57 (4H, q, $J = 7.0$ Hz), 4.17 (2H, t, $J = 7.2$ Hz), 1.71 (2H, m), 1.51 (6H, t, $J = 7.0$ Hz), 1.3−1.1 (10H, m), 0.81 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 164.10, 163.57, 148.11, 146.99, 146.10, 145.95, 145.50, 145.27, 145.24, 145.07, 145.05, 144.99, 144.59, 144.52, 144.08, 143.95, 143.03, 142.79, 142.56, 141.97, 141.94, 141.87, 141.80, 141.11, 140.93, 140.88, 140.39, 139.55, 139.17, 138.96, 135.00, 128.25, 125.77, 123.26, 122.87, 108.41, 71.17, 70.66, 69.70, 63.47, 50.16, 43.29, 31.78, 29.41, 29.14, 28.98, 27.31, 22.58, 14.30, 14.06; APCI MS *m/z* 1283 (M$^-$). **7**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.28 (1H, s), 8.14 (1H, d, $J = 7.6$ Hz), 7.98 (1H, s), 7.77 (1H, d, $J = 7.6$ Hz), 7.66 (1H, d, $J = 8.2$ Hz), 7.48 (1H, t, $J = 7.2$ Hz), 7.4−7.3 (5H, m), 7.12 (1H, t, $J = 7.2$ Hz), 7.00 (1H, d, $J = 8.5$ Hz), 6.55 (1H, d, $J = 8.2$ Hz), 5.96 (1H, d, $J = 11.3$ Hz), 5.66 (1H, d, $J = 11.3$ Hz), 5.52 (1H, d, $J = 11.3$ Hz), 5.50 (1H, d, $J = 11.3$ Hz), 4.58 (2H, q, $J = 7.2$ Hz), 4.51 (2H, q, $J = 7.2$ Hz), 4.40 (2H, m), 3.96 (2H, m), 3.77 (1H, m), 3.56 (1H, m), 3.34 (1H, m), 3.16 (1H, m), 1.52 (3H, t, $J = 7.2$ Hz), 1.47 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 164.11, 163.52, 163.24, 147.12, 146.80, 146.49, 146.43, 146.37, 146.33, 146.31, 146.24, 146.01, 145.88, 145.86, 145.74, 145.68, 145.58, 145.54, 145.37, 145.32, 145.15, 145.01, 144.98, 144.80, 144.33, 144.21, 144.15, 143.91, 143.54, 143.36, 143.19, 143.13, 143.09, 143.05, 143.01, 142.87, 142.84, 142.61, 142.27, 142.24, 141.87, 141.83, 141.66, 141.46, 141.30, 140.92, 140.74, 140.67, 140.59, 140.45, 140.29, 140.05, 139.14, 138.95, 138.57, 137.04, 136.56, 128.41, 128.21, 128.17, 126.16, 126.14, 125.66, 125.46, 123.06, 123.05, 122.84, 122.83, 122.38, 120.67, 120.38, 119.62, 119.35, 109.17, 108.90, 108.76, 107.82, 71.50, 71.18, 71.00, 70.89, 70.28, 69.82, 69.28, 69.13, 63.50, 63.35, 51.48, 51.20, 43.39, 42.37, 14.30, 14.26; APCI MS *m/z* 1408 (M$^-$).

proton peaks, and one set of AB quartet due to benzyl protons, obviously indicating the presence of C_2 or C_s symmetry.[8] The malonate methylene protons were missing in **5**. These spectral patterns apparently contrast with those of **6**. The observation of benzyl protons as an AB quartet suggests the conformational rigidity in **5**. The addition sites of **5** could not be disclosed by the NMR spectra alone. The UV−vis spectrum of **5** exhibits two broad bands between 600 and 700 nm, which are characteristic of trans-4 bisadducts formed by Bingel reaction in the literature.[9] For the trans-4 bisadduct, three diastereoisomers are possible, with respect to the orientation of ethoxycarbonyl groups on the methano bridges.[10] Among them, the diastereoisomer with two ethoxycarbonyl groups directed outside is the most stable, according to MM2 calculations. Hence, **5** was definitely assigned to the structure depicted in Scheme 3. The MM2 calculations also suggest that this trans-4 isomer is the most stable among the bisadduct regioisomers and diastereoisomers derived from **2**. Even the second stable *e* isomer is less stable than the trans-4 by 4 kcal/mol. It is likely that the carbazole residue as a spacer between two malonate ester moieties in **2** makes the *trans*-4 bisaddition more favorable.

The Bingel reaction using **3** under the conditions similar to **2** gave two bisadduct regioisomers **7** and **8** in 15 and 6% yields (based on the consumed [60]fullerene (78%)), respectively, in addition to monoadduct **9** (Scheme 4). Both isomers **7** and **8** were successfully separated and isolated by HPLC using a Develosil RPFULLERENE column (eluent: toluene/acetonitrile (3:7 (v/v))). The ^{1}H NMR spectra of both **7** and **8** exhibited complex spectral patterns suggesting C_1 symmetry; more than seven aromatic proton peaks and two sets of ethyl proton peaks were detected.[8] The UV−vis spectra of **7** and **8** were quite similar to those of trans-3 and *e* isomers, respectively, modified by Bingel reaction in the literature.[9] Thus, it is reasonable to assign **7** and **8** to trans-3 and *e* bisadducts, respectively. This assignment is consistent with their elution order; it was previously reported that, on this HPLC column, the regioisomers with addends at more remote positions eluted at earlier retention times.[11] The trans-3 bisaddition can afford three diastereoisomers, depending on the orientation of two ethoxycarbonyl groups, as in trans-4. Among them, one isomer has C_1 symmetry, in which one of two ethoxycarbonyl groups is directed inside and the other directed outside (abbreviated as in−out), whereas the other two isomers have C_2 symmetry (in−in and out−out). Hence, bisadduct **7** is assignable as the C_1-symmetrical trans-3 diastereoisomer (in−out). The two diastereoisomers possible for *e* bisadduct both adopt C_1 symmetry. The formation of trans-3 and *e* bisadducts from **3** is rather reasonable, since these regioisomers could be predominantly obtained in typical Bingel bisaddition without steric restraint,[9,12] and the spacer unit bridging two malonate ester moieties in **3** is much more flexible than that in **2**.

Scheme 4. Bingel Reactions Using **3**



In the carbazole-linked fullerene adducts obtained, the relative arrangements between the two chromophores are different from one another, which can affect photophysical processes such as photoinduced electron transfer. As preliminary investigation on their photophysical properties, fluorescence spectra of monoadduct **4** and trans-4 bisadduct **5** were measured in toluene/acetonitrile (1:1 (v/v)) at room temperature. With 430 nm excitation, which can produce the excited state (S_1) of [60]fullerene moiety exclusively, only quite weak and broad fluorescence derived from the [60]fullerene moiety was observed around 700 nm.[13] The carbazole fluorescence was almost quenched, even in the UV region excitation (e.g., 300 nm), which can afford the excited state (S_1) of the carbazole moiety as well as the [60]fullerene moiety. This quenching is probably ascribed to the intramolecular energy and/or electron transfer from the carbazole moiety to the fullerene moiety, although more detailed photophysical measurements such as transient absorption spectra are necessary for the quantitative interpretation. Such investigation is now in progress.

Acknowledgment. This work was financially supported by grants from The Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of [60]fullerene adducts **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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