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Regio- and diastereo-controlled synthesis of bis(formylmethano)[60]fullerenes and their application to the formation of [60]fullerene pearl-necklace polyimines

Hiroshi Ito, Yasuhiro Ishida and Kazuhiko Saigo*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Abstract—The tether-directed method was firstly applied to the biscyclopropanation of [60]fullerene via the addition–elimination reaction of bis(sulfonium ylide)s to give bis(formylmethano)[60]fullerenes with satisfactory regio- and stereoselectivity. The *equatorial*bisadduct thus obtained was used for the polycondensation with an aromatic diamine to afford the corresponding pearl-necklace polyimine with satisfactorily high degree of polymerization.

The attractive structure and properties of fullerenes have driven chemists to apply them and/or their derivatives in various fields.[1] From the viewpoint of materials science and technology, the synthesis of fullerene-containing polymers is a key issue to improve the processability of fullerenes without harming their unique properties. Fullerene-containing polymers can be roughly classified into two categories, main-chain type and side-chain type.[2–4] Among them, polymers containing fullerene cores in their main chain, so-called pearl-necklace polymers, are of great interest owing to their unique structure; chromophores are arrayed in a sequence-regulated manner along with the direction of the main chain. For the creation of such pearl-necklace polymers, the preparation of bifunctionalized fullerenes is indispensable. Even at present, however, pearl-necklace polymers have been rarely reported, mainly because of difficulty in the preparation of structurally ordered, bifunctionalized fullerenes.[3]

As a part of our ongoing program to develop fullerene-containing functional polymers, we have reported the synthesis and properties of [60]fullerene (C_{60}) pearl-necklace polyamides by the condensation of a regio- and diastereo-regulated bis(carboxymethano)C_{60} with aromatic diamines.[4] The resultant polyamides were of particular interest, owing to the special properties of the bridge-head carbons of the cyclopropane rings; the C_{60} cores and the carbonyl functions, embedded in the main chain, might conjugate through the cyclopropane carbons having an sp^2-character to some extent, which arises from the highly distorted structure of the cyclopropane rings. On the other hand, in order to develop a novel building block for C_{60}-containing functional materials other than carboxymethano C_{60} derivatives, we have investigated the synthesis and reactions of a C_{60} derivative with a formylmethano group;[5] the formylmethano C_{60}, prepared by the nucleophilic addition and elimination of a sulfonium ylide, could efficiently condense with aromatic amines to afford imine bond-connected C_{60}-aromatic ring arrays, for which photo-induced electron transfer between the C_{60} core and the aromatic group was observed. These results indicate that C_{60} derivatives with two formylmethano groups would be attractive monomers, which should easily give polyimines by the condensation with aromatic diamines. Compared with the carboxyl groups in bis(carboxymethano)C_{60}s, formylmethano groups might be introduced to a C_{60} core without any protecting group, and their sufficient reactivity would allow us to use the formyl groups directly for a polycondensation. Furthermore, the resultant polyimines were expected to be

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Keywords: Bifunctionalization; Formyl group; Fullerene; Polyimine; Template synthesis.

* Corresponding author. Tel.: +81 3 5841 7267; fax: +81 3 5802 3348; e-mail: saigo@chiral.t.u-tokyo.ac.jp

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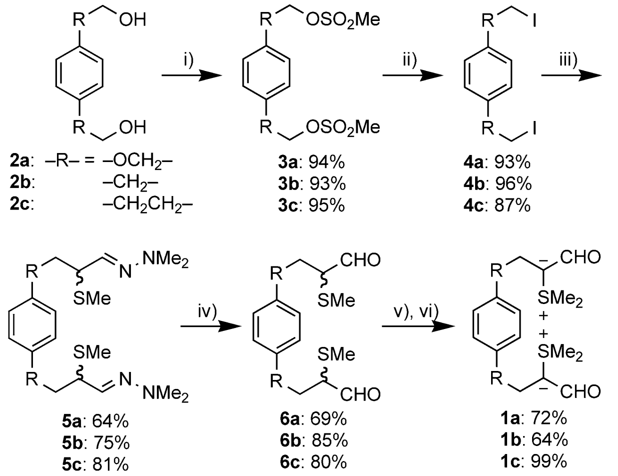
more fascinating materials for the development of novel electrochemical and optical devices, considering the fully conjugated structure of the azomethine units and aromatic rings.[6] Here we report the regio- and diastereoselective synthesis of bis(formylmethano)C_{60}s and their successful condensation with an aromatic diamine to generate novel C_{60} pearl-necklace polyimines.

In order to regio- and diastereoselectively introduce two formylmethano groups on a C_{60} core, we attempted to apply the tether-directed bifunctionalization strategy, which is known to be applicable to various kinds of C_{60} functionalization reactions, such as the Bingel reaction, [4+2] cycloaddition, and [3+2] cycloaddition.[7,8] Up to present, however, tether-directed method has not been applied to the biscyclopropanation with bis(sulfonium ylide)s, even though some functional groups including a formyl group can be introduced only by this method. Therefore, we designed three bis(α-formylsulfonium ylide)s **1a–c** in order to achieve regio- and diastereo-controlled synthesis of bis(formylmethano)C_{60}s. As the core part of **1a–c**, a 1,4-phenylene moiety was used, because bismalonates with a similar tethered structure have been known to realize the highly regio- and diastereo-controlled double Bingel reaction.[7] The bis(α-formylsulfonium ylide)s **1a–c** were successfully synthesized as follows (Scheme 1): The diols **2a–c** were converted to the dimesylates **3a–c** (93–95%), which were then transformed to the diiodides **4a–c** (87–96%). The diiodides **4a–c** were treated with a lithium enolate, generated from (methylthio)acetaldehyde *N*,*N*-dimethylhydrazone, to afford the bis(α-sulfenylated hydrazone)s **5a–c** (64–81%). The bis(α-sulfenylated hydrazone)s **5a–c** thus obtained were hydrolyzed with an aqueous hydrochloric acid solution to give the corresponding α,α′-disulfenylated dialdehydes **6a–c** (69–85%). Finally, the α,α′-disulfenylated dialdehydes **6a–c** were bismethylated with Me_3OBF_4, and the resultant bis(sulfonium tetrafluoroborate)s were treated with an aqueous alkaline solution to give the corresponding bis(α-formylsulfonium ylide)s **1a–c** (64–99%, two steps).[9]

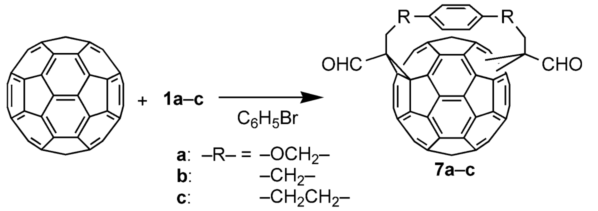
The bis(α-formylsulfonium ylide) **1a** derived from hydroquinone was used for the biscyclopropanation at rt. Unfortunately, however, C_{60} was not consumed at all (Table 1, entry 1). Even when the reaction was conducted at 80 °C, only a product with high polarity was generated. The spectroscopic analyses of the unidentified product with MALDI-TOF-MS and ^1H NMR suggested that only one of the two sulfonium ylide moieties in **1a** participated in the cyclopropanation and the other decomposed (entry 2). The oxygens adjacent to the phenylene core are likely to decrease the flexibility of the tether part, probably due to the partial conjugation with the aromatic ring. As a result, the monocyclopropanated C_{60} generated by the first addition might be not able to take a suitable conformation for the second intramolecular cyclopropanation. With the result in mind, we next attempted the cyclopropanation with bis(α-formylsulfonium ylide) **1b** possessing ethylene spacers between the phenylene core and the sulfonium ylide units. When the reaction was conducted at rt, unreacted C_{60} was recovered quantitatively once again (entry 3). To our delight, the reaction proceeded with moderate efficiency and excellent selectivity at a higher temperature (80 °C); the *cis*-3 bisadduct (*cis*-3-**7b**) was exclusively afforded (17% yield), accompanied with the formation of a trace amount of *cis*-2-**7b** (entry 4).[10,11] Quite interestingly, the predominant formation of the *cis*-3 isomer thus observed was completely opposite to our expectation; in the tandem biscyclopropanation of C_{60} with a monodentate α-folmylsulfonium ylide, the *cis*-1 and *cis*-3 bisadducts were not generated at all among the possible regio-isomers.[5b] Therefore, the notable regioselectivity was undoubtedly attributable to the constraint of the tether.

In order to improve the yield of bis(formylmethano)C_{60}s, the bis(α-formylsulfonium ylide) **1c** with relatively long spacers was then employed. As we expected,



Scheme 1. Synthesis of bis(α-formylsufonium ylide)s **1a–c**. Reagents and conditions: (i) MsCl, pyridine, CH_2Cl_2, 0 °C; (ii) NaI, acetone, reflux; (iii) (Methylthio)acetaldehyde *N*,*N*-dimethylhydrazone, LDA, THF, −78 °C; (iv) 6 M HCl aq., C_6H_6; (v) Me_3OBF_4, CH_2Cl_2; (vi) 12.5 M NaOH and satd K_2CO_3 aq., $CHCl_3$.

Table 1. Biscyclopropanation of C_{60} with **1a–c**



Entry	Ylide	Temp.	Isolated yield[a]			
			cis-2	*cis*-3	*equatorial*	*trans*-4
1	**1a**	rt	(no reaction)			
2[b]	**1a**	80 °C	—	—	—	—
3	**1b**	rt	(no reaction)			
4	**1b**	80 °C	trace	17	—	—
5	**1c**	rt	—	23	12	—
6	**1c**	80 °C	—	9	30	trace

[a] — Not detected.

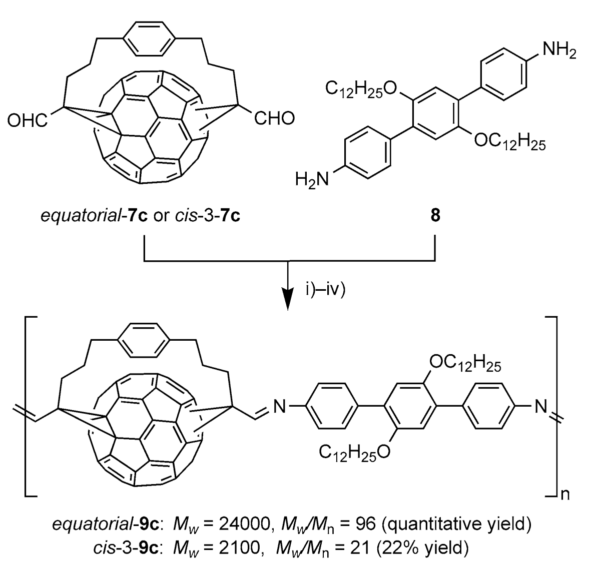
[b] The monocyclopropanated C_{60} was generated in <5% yield.

the reaction proceeded smoothly at 80 °C to give mainly a mixture of bisadducts. From the reaction mixture, the *cis*-3 and *equatorial* bisadducts (*cis*-3-**7c** and *equatorial*-**7c**) were easily isolated in 9% and 30% yields, respectively, by using preparative TLC (entry 6).[10,11] The difference in regioselectivity between the reaction with **1b** and that with **1c** is in good agreement with the length and flexibility of their spacers. Worth to note is the fact that **1c** could react with C_{60} even at room temperature, which was in sharp contrast to the cases of **1a** and **1b**; the *cis*-3 and *equatorial* bisadducts were again predominantly generated in 23% and 12% yields, respectively (entry 5). Considering the fact that the reactions with **1a** and **1b** did not afford monocyclopropanated C_{60}s at a detectable level, these observations might be elucidated by the difference in the inherent reactivity of the sulfonium ylides rather than the mobility of the linkers; the slight structural modification of a sulfonium ylide results in the significant change in the reactivity, which is in good agreement with our previous results.[5a] Furthermore, in the reactions of **1c**, the regioselectivity could be switched by changing the reaction temperature (entries 5 and 6). The observed change in regioselectivity indicates that the *cis*-3 bisadduct was the kinetic-controlled product whereas the *equatorial* bisadduct was the thermodynamic-controlled one.[12]

Thus, three kinds of bis(formylmethano)C_{60}s with a well-defined structure, *cis*-3-**7b**, *cis*-3-**7c**, and *equatorial*-**7c**, could be prepared. Considering the potential transformation of formyl groups into other functional groups, such as acetals, imines, alkenes, alcohols, etc., the bis(formylmethano)C_{60}s thus obtained are expected to be applied as fundamental building blocks for C_{60}-containing functional materials.

All of the bis(formylmethano)C_{60}s thus obtained were potential monomers for the polycondensation with aromatic diamines to form C_{60} pearl-necklace polyimines. As the initial study on the synthesis of the polyimines, we selected *equatorial*-**7c** as the monomer, because of its high yield in preparation and because of its high solubility compared with the other bisadducts. On the other hand, the aromatic diamine should be carefully selected, because the resultant polyimine was worried to be a material with poor solubility due to the rigid structures of the C_{60} core, diamine moiety, and imine bond. Therefore, we used an aromatic diamine with two long alkyl chains, 4,4″-diamino-2′,5′-bis(dodecyloxy)-*p*-terphenyl (**8**).

For the polycondensation of *equatorial*-**7c** with **8**, several methods were attempted, and finally we found that the combination of $TiCl_4$ and 1,4-diazabicyclo-[2.2.2]octane (DABCO) was quite efficient for the polyimine formation (Scheme 2).[13] By using monofunctionalized analogues, we confirmed that the condensation did not cause any detectable side reactions. When the polycondensation of *equatorial*-**7c** with **8** was carried out in benzene, the polymeric *equatorial*-**9c** was obtained quantitatively.[9] A GPC analysis revealed that the mean molecular weight was satisfactorily high ($M_w = 24{,}000$, $M_w/M_n = 96$).[14] As we had worried, however, the solubility of the C_{60} monomers significantly affected the efficiency of the polycondensation; for example, the polycondensation of *cis*-3-**7c**, of which the solubility was lower than that of *equatorial*-**7c**, with **8** under the same conditions caused the precipitation of oligomeric *cis*-3-**9c** at a quite early stage of the polycondensation to prevent further chain elongation. As a result, only a mixture of oligomers with insufficient degree of polymerization was recovered in poor yield.



Scheme 2. Polycondensation of bis(formylmethano)C_{60}s **7c** with diamine **8**. Reagents and conditions: (i) $TiCl_4$ (10 equiv), DABCO (40 equiv), reflux in C_6H_6, 5 h; (ii) Filtration; (iii) Successive extraction with $CHCl_3$, CS_2, and C_6H_5Cl; (iv) Reprecipitation with MeOH from a CS_2 solution.

The FT-IR and ^1H NMR spectra of polymeric *equatorial*-**9c**, obtained by polycondensation in benzene, clearly showed that the formyl groups were transformed to the corresponding imino groups in high conversion.[9] In the ^1H NMR spectrum, every signal was observed as a broad peak but completely assigned to the protons in the repeating unit, as observed for polymers with a sufficient degree of polymerization. In addition, no detectable signal was observed around 6.5 ppm, strongly suggesting that the undesired nucleophilic attack of the diamine to the C_{60} core hardly occurred.[15] Worth to note is the excellent processability of the pearl-necklace polyimine, *equatorial*-**9c**. In general, carbon clusters are prone to form self-aggregated domains, which is a serious obstacle in the full reflection of their characteristic properties in carbon cluster-containing devices. However, an isotropic thin film could be easily obtained from the pearl-necklace *equatorial*-**9c**. For example, the cast of a solution of the polyimine *equatorial*-**9c** in CS_2 on a glass plate, followed by the slow evaporation of the solvent, gave a film, which could be detached from the glass plate. The homogeneity of the resultant film allowed its characterization by UV–vis absorption spectroscopy;[9] the absorption spectrum of the polymer thin film was quite similar to that of the polymer in a dilute solution, but slightly red-shifted most likely owing to the stacking of the chromophores.

In conclusion, we succeeded in the regio- and diastereoselective synthesis of bis(formylmethano)C_{60}, upon firstly applying the tether-directed bifunctionalization method for the biscyclopropanation of C_{60} with bis(sulfonium ylide)s. The addition pattern could be controlled by the structure of the biscyclopropanating reagents and the reaction temperature. Among the bis(formylmethano)C_{60}s thus obtained, *equatorial*-**7c** was found to be a fascinating monomer for the formation of regio- and diastereo-regulated pearl-necklace polymers by the polycondensation with aromatic diamines such as **8**. The corresponding high polymer could be obtained by using a $TiCl_4$/DABCO system. The resultant pearl-necklace polyimine, *equatorial*-**9c**, showed excellent processability, which would enable the creation of novel functional devises possessing polymeric C_{60} arrays.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.148.

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9. See Supplementary data.
10. The structural assignment of the C_{60} bisadducts **7b** and **7c** was conducted based on the ^{1}H and ^{13}C NMR spectra, UV–vis spectra, and the consideration of the distance between the two cyclopropane rings of each bisadduct with respect to the length of the tether moiety. See Supplementary data.
11. The tether-directed biscyclopropanation can afford several diastereoisomers with respect to the relative orientation of the formyl groups at the bridge-head carbons (*in–in*, *out–out*, *in–out*). Considering the distance between the two cyclopropane rings of **7b** and **7c** with respect to the length of the tether moieties, together with the symmetry deduced from ^{1}H and ^{13}C NMR spectroscopy, the *out–out* configuration was assigned for all of the bisadducts.
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