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Synthesis and transformation of a novel methano[60]fullerene having a formyl group

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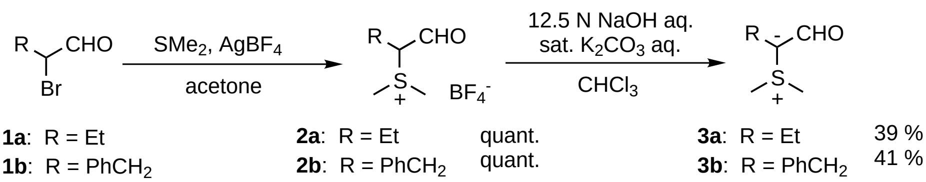
Abstract—The reaction of [60]fullerene with a dimethylsulfonium α-formylalkylide gave a novel methano[60]fullerene having a formyl group at the bridge-head carbon. This 2,2-[60]fulleroalkanal was readily converted into a variety of *N*-aryl-2,2-[60]fulleroaldimines by condensation with aromatic amines; one of them showed efficient quenching of the fluorescence of the [60]fullerene core, due to a photoinduced intramolecular electron transfer. © 2001 Elsevier Science Ltd. All rights reserved.

The functionalization of fullerenes has attracted considerable attention owing to the successful applications of the fullerene derivatives in materials science.[1] Among a large number of functionalized [60]fullerene derivatives, methano[60]fullerenes having carboxyl or carbonyl group(s) at the bridge-head carbon have been intensively studied and used as versatile building blocks for the construction of [60]fullerene-containing materials;[2] 2,2-[60]fulleroalkanoates, -alkanamides and -alkanones have been synthesized with the expectation that the [60]fullerene core and the carbonyl function would conjugate through the cyclopropane carbons, having a *p*-character to some extent.[3–6] However, the synthesis of 2,2-[60]fulleroalkanals has not hitherto been reported, even though a formyl group is well-known to be an important and useful functional group in organic synthesis, due to its high reactivity and facility in converting into other functional groups, such as an imino group by condensation with amines and an olefinic group by addition–elimination of carbanions and their equivalents. Thus, the introduction of a formyl substituent onto the bridge-head carbon of methano[60]fullerenes is synthetically interesting and would be a new approach for the synthesis of functionalized [60]fullerenes.

Several synthetic methods for methano[60]fullerenes have been developed; (1) the addition-eliminations of α-halocarbanions, the so-called Bingel reaction,[3] and of sulfonium ylides,[4] (2) the addition–thermal decomposition of diazo compounds[5] and (3) the addition of free carbenes.[6] Among them, the reaction of [60]fullerene with stabilized sulfonium ylides is less frequently applied than the other methods in the synthesis of methano[60]fullerenes, although the reaction provides a convenient route to the preparation of methano[60]fullerenes having carbonyl group(s) at the bridge-head carbon. We report herein the synthesis of a new methano[60]fullerene derivative, having a formyl group at the bridge-head carbon, by the reaction of [60]fullerene with a stabilized dimethylsulfonium α-formylalkylide, together with its transformation into *N*-arylaldimines, which could be applied to the construction of [60]fullerene–electron donor dyad systems.



Scheme 1.

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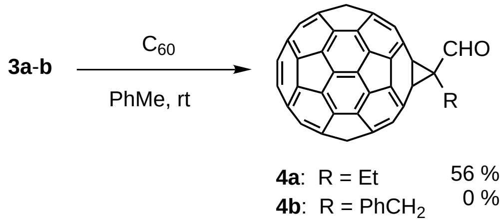
Treatment of (α-formylalkyl)dimethylsulfonium tetrafluoroborates **2a**–**b**, which were prepared from the corresponding α-bromoaldehydes **1a**–**b**, SMe_2 and $AgBF_4$, with a mixture of 12.5 M aq. NaOH and saturated aq. K_2CO_3 gave the corresponding stabilized dimethylsulfonium α-formylalkylides **3a**–**b** (Scheme 1).[7] To a solution of [60]fullerene in toluene was added a toluene solution of 2 equimolar amounts of ylide **3a**–**b**. Ylide **3a** smoothly underwent an addition–elimination reaction with [60]fullerene at rt to give 2,2-[60]fullerobutanal **4a** in moderate yield after purification by chromatography on silica gel (Scheme 2).[8] In contrast, the reaction of ylide **3b** with [60]fullerene did not proceed at all even at 100°C, and unreacted [60]fullerene was quantitatively recovered; the addition of ylide **3b** to [60]fullerene would be suppressed due to the steric repulsion between the [60]fullerene core and the benzyl group of **3b** and/or due to the formation of the less reactive dimethylsulfonium enolate. These results indicate that the cyclopropanation of [60]fullerene with stabilized dimethylsulfonium α-formylalkylides would be a new route to the synthesis of methano[60]fullerenes having a formyl group at the bridge-head carbon.

We next attempted conversion of 2,2-[60]fullerobutanal **4a** into the corresponding aldimines. The reaction of **4a** with an equimolar amount of several kinds of aromatic amines, having electron-donating substituent(s) on the benzene ring, was carried out in benzene in the presence of 4 Å MS. In all cases, the condensation proceeded smoothly, and the desired *N*-aryl-2,2-[60]fulleroaldimines **5a**–**e** were obtained in quantitative yields (Scheme 3).[9] These *N*-aryl-2,2-[60]fulleroaldimines could be purified by recrystallization from a mixture of chloroform and hexane.

The UV–vis absorption spectra of 2,2-[60]-fullerobutanal **4a** and *N*-aryl-2,2-[60]fulleroaldimines **5a**–**e** in dichloromethane exhibited similar patterns (Fig. 1), indicating that an intramolecular charge transfer interaction is negligible in the ground state. The fluorescence spectra of **4a** and **5a**–**e** were also measured upon exciting them with a wavelength of 410 nm (excited only the [60]fullerene core) in dichloromethane at the same absorbance (Abs. = 0.3) (Fig. 2). Virtually identical fluorescence peaks were observed at about 700 nm with almost the same intensity for **4a** and **5a**–**d**. In contrast, in the case of **5e** having a dimethylamino substituent, the efficient quenching of its fluorescence was observed. This quenching indicates that a photoinduced intramolecular electron transfer sufficiently occurs from the electron-donating aromatic ring to the excited singlet state of the [60]fullerene core.[10]

In conclusion, we have found that a new methano[60]fullerene, having a formyl group, could be prepared by the reaction of [60]fullerene with a stabilized dimethylsulfonium α-formylalkylide and transformed into the corresponding *N*-arylaldimines, which are a new kind of donor–acceptor dyads containing [60]fullerene, by the condensation with aromatic amines. This novel transformation of the 2,2-[60]fulleroalkanal is expected to be a clue to the introduction of new components onto a [60]fullerene core.



Scheme 2.

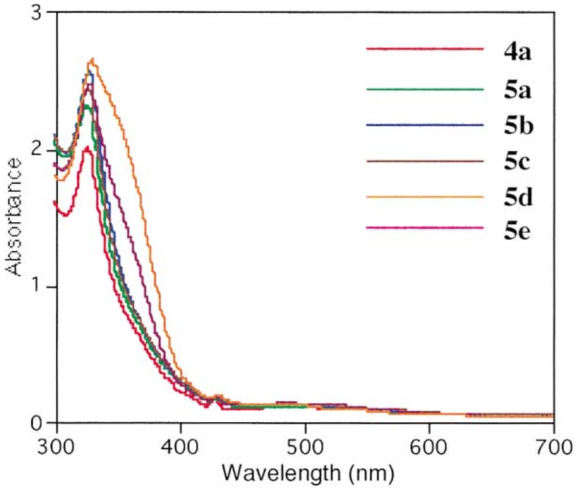
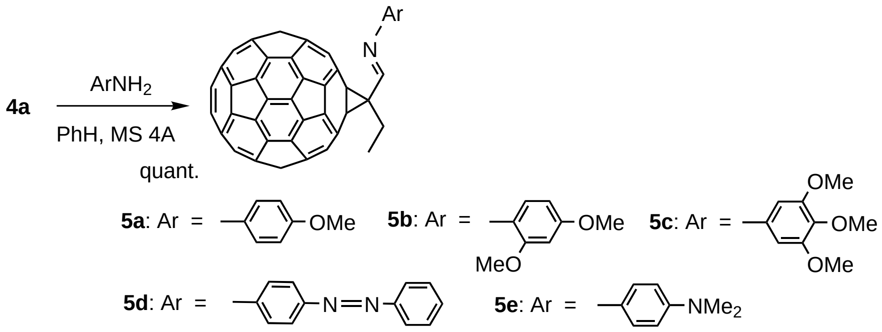


Figure 1. Absorption spectra of **4a** and **5a**–**e** in CH_2Cl_2 (5.0×10^{-5} M).



Scheme 3.

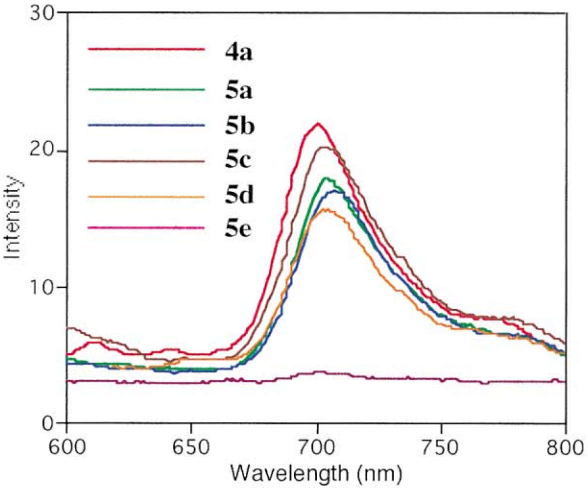


Figure 2. Fluorescence spectra of **4a** and **5a**–**e** upon exciting with a wavelength of 410 nm in CH_2Cl_2 at the same absorbance (Abs. = 0.3).

Acknowledgements

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7. A typical procedure for the preparation of dimethylsulfonium alkylides **3**: A mixture of α-bromobutanal **1a** (0.8 g, 5.2 mmol), dimethyl sulfide (1.86 g, 30 mmol) and silver tetrafluoroborate (1.94 g, 10 mmol) in acetone (5 mL) was stirred for 2 days at room temperature under Ar. Silver bromide deposited was filtered off through a Celite pad and washed thoroughly with ethanol. The combined filtrates were concentrated under reduced pressure to give (α-formylpropyl)dimethylsulfonium tetrafluoroborate **2a** (quant.). After adding chloroform (15 mL) to the finely powdered sulfonium tetrafluoroborate, a mixture of saturated potassium carbonate solution (1.2 mL) and 12.5 M sodium hydroxide (0.8 mL) was added in one portion to the resultant suspension, stirred vigorously at 5–10°C with ice-bath cooling. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 15 min. After removal of the inorganic salts deposited by filtration, the filtrate was dried over potassium carbonate and sodium sulfate. The filtrate was concentrated under reduced pressure to give crude dimethylsulfonium α-formylpropylide **3a**. Recrystallization of the crude product from benzene gave pure **3a** (0.27 g, 2 mmol, 39%). ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz): The major isomer, 1.16 (t, $J=7.5$ Hz, 3H), 2.38 (q, $J=7.5$ Hz, 2H), 2.56 (s, 6H), 8.38 (s, 1H) ppm; the minor isomer, 1.03 (t, $J=7.5$ Hz, 3H), 2.20 (q, $J=7.5$ Hz, 2H), 2.96 (s, 6H), 8.50 (s, 1H) ppm. ^{13}C NMR ($CDCl_3/CS_2$, 75 MHz): 14.85, 15.57, 30.24, 79.01, 173.20 ppm. IR (KBr): 1560 (C=O) cm^{-1}.
8. The synthesis of 2,2-[60]fullerobutanal **4a**: To a solution of [60]fullerene (36 mg, 0.05 mmol) in dry toluene (45 mL) was added dimethylsulfonium α-formylpropylide **3a** (13.2 mg, 0.1 mmol). After the solution was stirred at rt for 20 h under Ar, the reaction mixture was directly chromatographed on silica gel (eluent: hexane to dichloromethane) to give 2,2-[60]fullerobutanal **4a** (22 mg, 0.028 mmol, 56%). ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz): 1.52 (t, $J=7.2$ Hz, 3H), 2.86 (q, $J=7.2$ Hz, 2H), 10.56 (s, 1H) ppm. ^{13}C NMR ($CDCl_3/CS_2$, 75 MHz): 12.12, 19.33, 50.81, 75.06, 137.68, 137.86, 140.92, 141.41, 141.82, 141.84, 141.87, 141.91, 142.81, 142.89, 142.93, 143.55, 143.62, 144.28, 144.44, 144.46, 144.50, 144.52, 144.55, 144.84, 145.00, 145.01, 145.09, 145.11, 145.56, 146.56, 193.05 ppm. IR (KBr): 1720 (C=O), 525 (C_{60}) cm^{-1}. FAB-MS: 790 (M$^+$).
9. A typical procedure for the synthesis of *N*-aryl-2,2-[60]fulleroaldimines **5**: To a solution of 2,2-[60]fulleroabutanal **4a** (47.4 mg, 0.06 mmol) in dry benzene (30 mL) was added *p*-methoxyaniline (7.38 mg, 0.06 mmol) and 4 Å MS (1.5 g) at room temperature. After the solution was stirred for 2 days under Ar, the 4 Å MS was filtered off through a Celite pad and washed with dichloromethane. The combined filtrates were concentrated under reduced pressure to give *N*-(*p*-methoxyphenyl)-2,2-[60]fullerobutyroaldimine **5a** (quant.). Recrystallization of the product from $CHCl_3$/hexane gave pure **5a**. ^{1}H NMR ($CDCl_3/CS_2$, 300 MHz): 1.62 (t, $J=7.2$ Hz, 3H), 3.05 (q, $J=7.2$ Hz, 2H), 3.86 (s, 3H), 6.98 (d, $J=8.7$ Hz, 2H), 7.29 (d, $J=9.0$ Hz, 2H), 8.85 (s, 1H) ppm. ^{13}C NMR ($CDCl_3/CS_2$, 75 MHz): 12.12, 20.98, 48.76, 55.45, 78.26, 114.49, 122.21, 137.22, 138.0, 141.04, 141.98, 142.08, 142.12, 142.17, 142.96, 143.04, 143.14, 143.78, 144.02, 144.19, 144.28, 144.46, 144.54, 144.72, 144.75, 144.83, 145.10, 145.20, 145.24, 145.55, 145.61, 147.68 ppm. IR (KBr): 1640 (C=N), 1500 (Ar), 1250 (MeO), 523 (C_{60}) cm^{-1}. FAB-MS: 895 (M$^+$).
10. A similar quenching was not observed in the fluorescence measurement of the mixture of **4a** and *N*,*N*-dimethylaniline under the identical conditions.