ARTICLE

OBC
www.rsc.org/obc

Formation of fulleroids as major products and application of solid state reaction in the functionalization of [60]fullerene by aromatic diazoketones

Yosuke Nakamura,[a] Ken'ichi Inamura,[a] Ryosuke Oomuro,[a] Richard Laurenco,[b] Thomas T. Tidwell[b] and Jun Nishimura*[a]

[a] *Department of Nano-Material Systems, Graduate School of Engineering, Gunma University, Kiryu, Gunma, 376-8515, Japan. E-mail: nisimura@chem.gunma-u.ac.jp; Fax: 81-277-30-1314; Tel: 81-277-30-1310*

[b] *Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada*

Received 20th April 2005, Accepted 8th June 2005

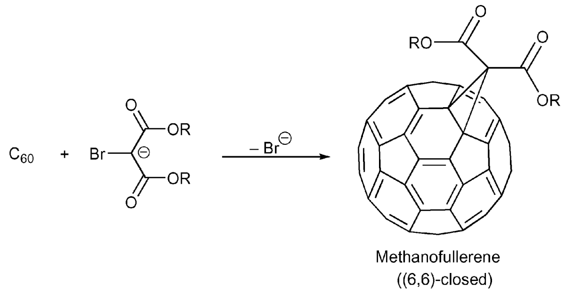
First published as an Advance Article on the web 11th July 2005

The reactions of various aromatic diazoketones with [60]fullerene were investigated in solution (*o*-dichlorobenzene) or in the solid-state. Under all the conditions examined, the fulleroid with the methine proton located over a six-membered ring was obtained as a major product along with a slight amount of the other fulleroid diastereoisomer and methanofullerene. Solid-state reactions considerably enhanced the reaction efficiency with minor effects on the selectivity. The thermal isomerization and photoisomerization from fulleroids into methanofullerene were relatively slow, almost independent of substituents under the conditions examined.

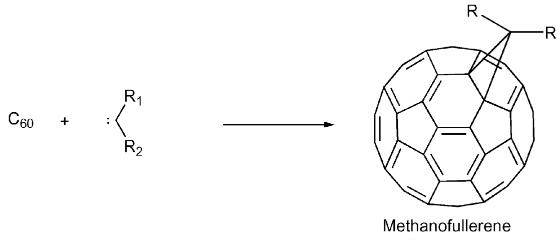
Introduction

Over the past decade, the reactivity of [60]fullerene has been extensively investigated, and a variety of fullerene adducts have been available.[1] Most addends attack (6,6)-junctions (bonds between two six-membered rings) of [60]fullerene rather than (5,6)-junctions (bonds between a six-membered ring and a five-membered ring).

Cycloaddition reactions, especially cyclopropanations, are most frequently employed for the fullerene functionalization.[2] Bingel reaction (the addition of stabilized α-halocarbanion to [60]fullerene, followed by intramolecular displacement of halide by the anionic center generated on the fullerene surface)[2a] and addition of carbenes generated from various precursors are typical examples for cyclopropanations (eqn. 1 and 2). These reactions exclusively afford "methanofullerenes" with (6,6)-closed structure.



(1)



(2)

In contrast, some reactions produce "fulleroids" with (5,6)-open structure, the isomer of methanofullerenes.[1,3,4] The addition of diazomethane to [60]fullerene is reported to give an unstable pyrazoline *via* 1,3-dipolar cycloaddition (Scheme 1).[3] The thermolysis of the pyrazoline afforded fulleroid quantitatively by nitrogen extrusion,[3] while photolysis of the pyrazoline gave both fulleroid and methanofullerene in a 4 : 3 ratio.[4]

In contrast with methanofullerenes possessing 58 π-electrons due to the loss of one double bond from the parent [60]fullerene, fulleroids still retain the 60 π-electron system similar to [60]fullerene itself, virtually preserving the electronic and electrochemical properties of [60]fullerene. Hence, in the functionalization of [60]fullerene, it is desirable to produce fulleroids rather than methanofullerenes, as the former are better suited for application in functional materials.[5]

However, most fulleroids bearing substituent(s) on the bridge carbon atom are readily converted into the corresponding methanofullerenes by thermal,[6] photochemical,[7] or electrochemical processes,[8] although the unsubstitued parent fulleroid (Scheme 1) is not isomerized into the methanofullerene.[4] Thus, in most reactions, it is difficult to obtain and isolate fulleroids as major products, even though fulleroids are preferentially produced.

In this study, we focused on the functionalization by various aromatic diazoketones **1a**–**c** under mild conditions, in pursuit of the reactions which can give fulleroids as the major products *via* pyrazolines. The reaction of diazoketone **1b** with [60]fullerene at 100–150 °C was reported in the literature;[9] it gave methanofullerene **4b** and dihydrofuran-fused fullerene derivative without the formation of fulleroid **2b** or **3b**. Here, the electronic and steric effects of **1a**–**c** on the yields and product distribution are revealed. To increase the reaction efficiency, solid-state reactions were also examined in addition to the conventional solution reactions. Furthermore, thermal and photochemical isomerization of fulleroids into methanofullerenes were investigated.

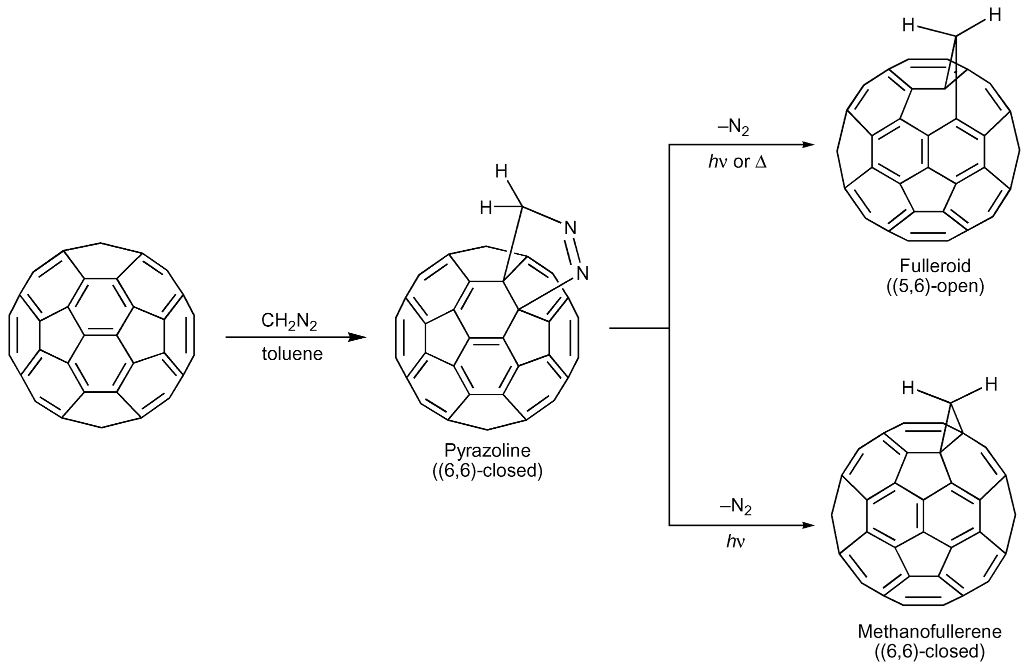
Results and discussions

Reactions between [60]fullerene and 1a–c in solution

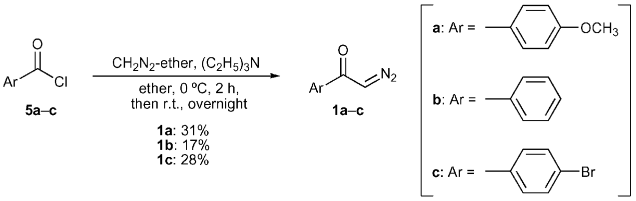
Diazoketones **1a**–**c** were synthesized by the reaction of the corresponding commercially available acid chlorides with diazomethane (Scheme 2).[10,11]

First, the reactions of [60]fullerene with **1a**–**c** (1.1 equiv.) were carried out in *o*-dichlorobenzene (ODCB) at 25 °C for two weeks. These reactions afforded mainly three products (**2**, **3**, and **4**) in all the cases (Scheme 3). Under these reaction conditions,

DOI:10.1039/b505558j



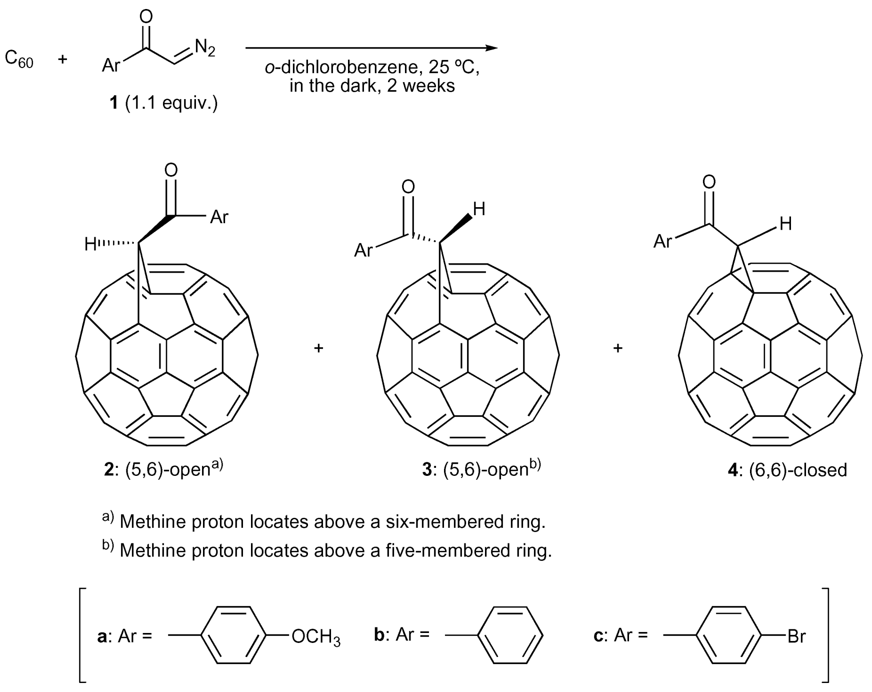
Scheme 1 Reaction between C_{60} and diazomethane.



Scheme 2 Synthesis of diazoketones **1a**, **1b** and **1c**.

no dihydrofuran-fused fullerene derivatives reported in the literature[9] were detected, since the reactions were performed at lower temperature. Both **2** and **3** are "fulleroids" with (5,6)-open structure, while **4** is a "methanofullerene" with (6,6)-closed structure. Fulleroids **2** and **3** are diastereoisomers to each other; the methine protons of **2** and **3** are located over a six-membered ring and five-membered ring, respectively. Although the mixture composed of **2**–**4** was separated from recovered [60]fullerene and other by-products by silica gel column chromatography and GPC (if necessary), the isolation of each of **2**–**4** was unsuccessful due to the similar polarity. Exceptionally, **2a** was isolated by repeated recrystallization. The isolated yields of mixtures **2**–**4** are summarized in Table 1.

Although the three products **2**–**4** have an identical molecular formula, their ^{1}H NMR spectra are expected to reveal quite different features from one another, because the methine protons of **2**–**4** are situated in quite different environments. It is reported that, in the unsubstitued fulleroid, the methylene protons resonate at δ 6.35 and δ 2.87 as two doublets, which are assigned to the proton above a five-membered ring and that above a



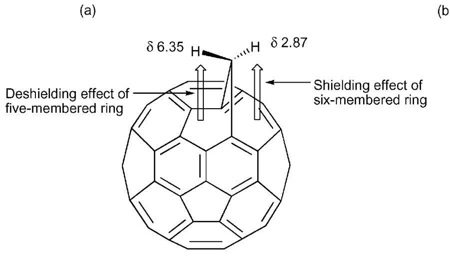
Scheme 3 Reaction of C_{60} with aromatic diazoketones **1** in *o*-dichlorobenzene.

Table 1 Results for reactions between [60]fullerene and **1a**–**c** in *o*-dichlorobenzene at 25 °C for two weeks

Diazoketone	Total yield of **2**–**4** (%)[a]	Ratio among **2**, **3**, and **4**[b]		
		2	**3**	**4**
1a	15 (19)	64	15	21
1b	5 (29)	65	18	17
1c	1 (26)	61	16	23

[a] Isolated yield. Yields based on consumed C_{60} are shown in parentheses. [b] Determined by the integral ratio of methine proton peaks.

six-membered ring, respectively, as shown in Scheme 4.[4] This difference is explained in terms of the deshielding effect of a five-membered ring and the shielding effect of a six-membered ring.[12] The methylene protons of (6,6)-closed methanofullerene are reported to resonate at δ 3.93 as a singlet.[4] Hence, the methine proton of fulleroid **2** is expected to resonate at rather high fields, while that of **3** at rather low fields, and that of **4** is in the middle region between them. The carbonyl group attached to the bridge carbon atom should induce a down-field shift on the methine protons similarly for all of **2**–**4**. As a representative example, the ^{1}H NMR spectrum of the mixture composed of **2a**–**4a** is illustrated in Fig. 1.



Scheme 4 Methylene protons of (a) fulleroid and (b) methanofullerene.

The isomer ratios among **2**–**4** were readily determined by the integral ratio of methine proton peaks, and are listed in Table 1. The ^{1}H NMR spectral data of **2**–**4** are summarized in Table 2. The chemical shifts for **4a** and **4b** were in close agreement with those in the literature.[13]

In all the cases examined, fulleroid **2** was obtained as the major product (61–65%), and fulleroid **3** was obtained in lesser amount (15–18%). This tendency is in agreement with those reported in the literature;[6,8a,14] the (5,6)-open diastereoisomer with the bulkier substituent located above the five-membered ring (*e.g.* **2**) is generally preferred. This selectivity is ascribed to less steric hindrance in the transition state leading to the major diastereoisomer from the precursor pyrazoline.[6,14] Thus, the ratio of the two diastereoisomers depends on the difference in bulkiness between the two substituents on the bridge carbon atom. The ratios of **2** and **3** resulting from **1a**–**c** are almost constant (*ca.* 4 : 1), suggesting that the *p*-substituents on the benzene ring hardly affect the steric hindrance.

Intriguingly, the total yields of **2**–**4** remarkably increase with increasing electron-donating property of substituents on the benzene ring of **1a**–**c**. Table 3 lists the AM1-calculated HOMO and LUMO energy levels for **1a**–**c** and [60]fullerene and the Hammett substituent constants (σ values) for the groups in **1a**–**c**.[15] The difference between the HOMO of **1a**–**c** and the LUMO of C_{60} and the σ values are clearly correlated with the isolated yields. Therefore, it is reasonable to interpret that these reactions proceed through the interaction between the HOMO of **1a**–**c** and LUMO of [60]fullerene.

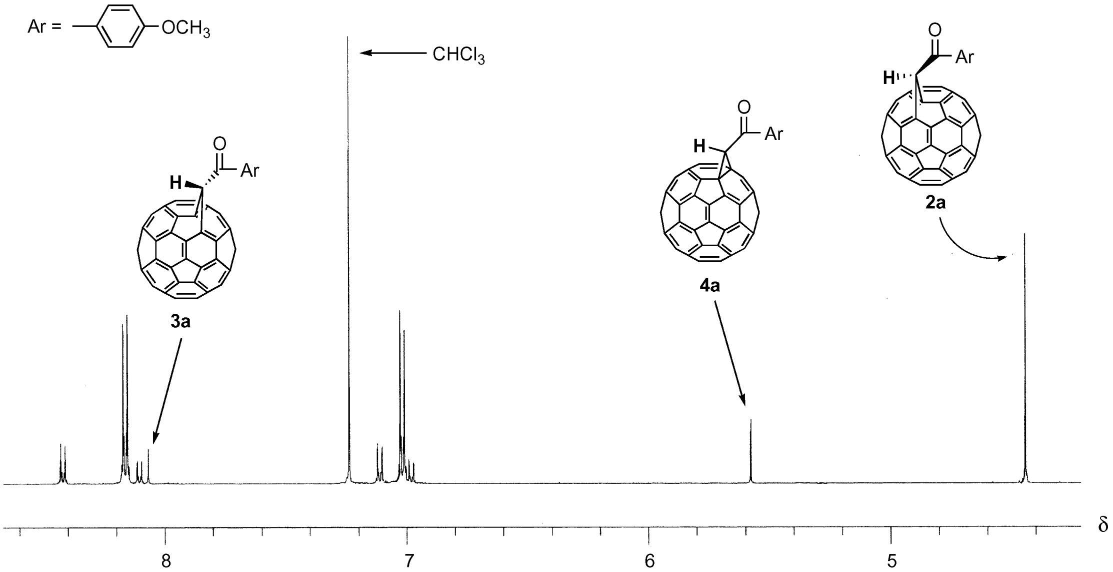


Fig. 1 ^{1}H NMR spectrum of mixture composed of **2a**–**4a** in $CDCl_3$–CS_2 (1 : 1).

Table 2 ^{1}H NMR Spectral data of **2**–**4**[a]

	Methine proton δ	Other protons δ
2a	4.43 (1 H, s)	8.16 (2 H, d, *J* 9), 7.02 (2 H, d, *J* 9), 3.92 (3 H, s)
3a	8.07 (1 H, s)	8.11 (2 H, d, *J* 9), 6.98 (2 H, d, *J* 9), 3.90 (3 H, s)
4a	5.59 (1 H, s)	8.42 (2 H, d, *J* 9), 7.11 (2 H, d, *J* 9), 3.96 (3 H, s)
2b	4.50 (1 H, s)	8.19 (2 H, d, *J* 7), 7.67 (1 H, t, *J* 7), 7.57 (2 H, t, *J* 7)
3b	8.11 (1 H, s)	8.14 (2 H, d, *J* 7), 7.62 (1 H, t, *J* 7), 7.53 (2 H, t, *J* 7)
4b	5.63 (1 H, s)	8.44 (2 H, d, *J* 7), 7.74 (1 H, t, *J* 7), 7.69 (2 H, t, *J* 7)
2c	4.37 (1 H, s)	8.06 (2 H, d, *J* 9), 7.71 (2 H, d, *J* 9)
3c	8.03 (1 H, s)	8.00 (2 H, d, *J* 9), 7.67 (2 H, d, *J* 9)
4c	5.52 (1 H, s)	8.31 (2 H, d, *J* 9), 7.80 (2 H, d, *J* 9)

[a] Measured in $CDCl_3$–CS_2 (1:1).

Table 3 AM1-Calculated HOMO and LUMO energy levels for **1a**–**c** and C_{60} and Hammett substituent constant (σ) for each substituent

	Total yields of **2**–**4** (%)	Orbital energy/eV		Difference between HOMO of **1** and LUMO of C_{60}/eV	σ
		HOMO	LUMO		
1a	15	−9.175	−0.390	6.23	−0.268
1b	5	−9.309	−0.427	6.36	0
1c	1	−9.443	−0.721	6.50	+0.232
C_{60}	—	−9.643	−2.947	—	—

As Table 1 shows, however, the total yields of **2**–**4** are not sufficiently high in solution reactions (only 15% even in case of **1a**), in spite of prolonged reaction time. It is undesirable to perform the reactions at higher temperatures or under photoirradiation, since fulleroids **2** and **3** appear to isomerize into methanofullerene **4** under these conditions. Therefore, for the purpose of enhancement of reaction efficiency, solid-state reactions were examined, as described below.

Solid-state reactions between [60]fullerene and 1a–c

As solid-state reactions, two methods (A and B) were employed. In Method A, a mixture of [60]fullerene and diazoketone **1** is manually ground by an agate mortar and pestle. Method B uses the high-speed vibration milling (HSVM) technique, which was developed by Komatsu *et al.*[16] Fig. 2 shows the HSVM apparatus, which was cordially fabricated by Nippon Gerotor Co., Ltd. A stainless steel capsule containing stainless steel milling balls and the reacting species fixed to this apparatus can be shaken by rapid vibration at the rate of 3000 revolutions per minute. This technique is expected to produce highly activated local sites in the reacting species due to the absence of any solvent molecules and to enable quite efficient and convenient mixing.

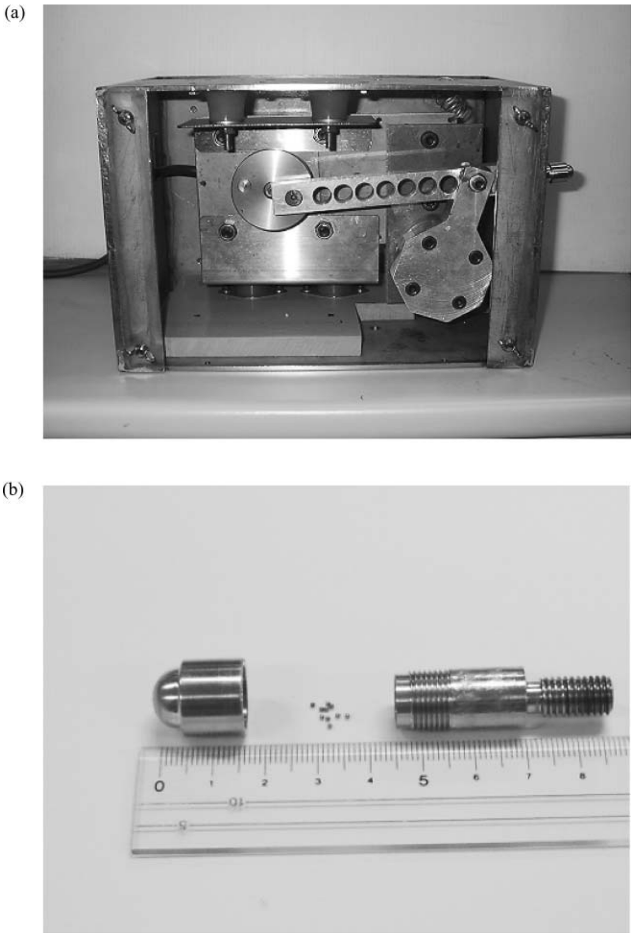


Fig. 2 Apparatus for HSVM used in the present study; (a) main body of HSVM; (b) stainless steel capsules and stainless steel milling balls.

Table 4 Results for solid-state reactions between [60]fullerene and **1a**–**c** by Method A (using an agate mortar and pestle) for 30 min

		Ratio among **2**, **3**, and **4**[b]		
Diazoketone	Total yield of **2**–**4**/%[a]	**2**	**3**	**4**
1a	18 (30)	63	30	7
1b	11 (38)	69	26	5
1c	5 (28)	73	19	8

[a] Isolated yield. Yields based on consumed C_{60} are shown in parentheses.
[b] Determined by the integral ratio of methine proton peaks.

First, the solid-state reactions between [60]fullerene and **1a**–**c** were performed by using an agate mortar and pestle (Method A) for 30 min, and the isolated yields of mixtures composed of **2**–**4** were determined after column chromatography, in a manner similar to the solution reactions. The isolated yields, along with the isomer ratios among **2**–**4** determined by the integral ratio of methine protons in ^1H NMR spectra, are listed in Table 4.

The total yields of **2**–**4** are increased compared to those obtained by the solution reactions shown in Table 1. The increase is remarkable, especially in the cases of **1b** and **1c**. It is obvious that this solid-state reaction considerably enhanced the reaction efficiency, since the reaction time is much shortened relative to that in solution reactions. In these cases, fulleroid **2** was again obtained as the major product, though the percentage of **3** slightly increased. It is probable that the increased reaction efficiency lowers the selectivity. Noticeably, the percentage of **4** decreased, probably due to the reduced formation from **2** and **3**, as described below.

The solid-state reactions of [60]fullerene with **1a**–**c** using HSVM technique (Method B) were carried out for an hour. In these and in all the cases of **a**–**c**, minor amounts of more polar products were also obtained in addition to **2**–**4**. These are evidently bisaddition products (bisadducts), resulting from the reaction of two molecules of diazoketones **1a**–**c** with one [60]fullerene molecule. Actually, the APCI mass spectra of crude products indicated the presence of bisadducts, and sometimes trisadducts. Since they were composed of complex regioisomeric mixtures, they were not subjected to further separation, and their yields were not determined. Only the total isolated yields of **2**–**4** and their isomer ratios were determined, and are listed in Table 5. In all the cases of **a**–**c**, the total yields of **2**–**4** are further increased compared to those obtained by Method A as well as solution reactions. Considering the formation of bisadducts, the actual conversions are expected to be still higher. The increase is

Table 5 Results for solid-state reactions between [60]fullerene and **1a**–**c** by Method B (using HSVM technique) for 1 h

		Ratio among **2**, **3**, and **4**[b]		
Diazoketone	Total yield of **2**–**4** (%)[a]	**2**	**3**	**4**
1a	20 (41)	67	23	10
1b	19 (38)	80	9	11
1c	15 (44)	77	13	10

[a] Isolated yield. Yields based on consumed C_{60} are shown in parentheses.
[b] Determined by the integral ratio of methine proton peaks.

especially remarkable in the case of **1c**. As a result, the difference in the total yields among **a**, **b**, and **c** became small. The ratio of **4** is low, similar to that by Method A. It is emphasized that, by using HSVM technique, solid-state reactions can be performed more conveniently; the HSVM technique enabled the efficient reaction without manually grinding reactants by an agate mortar and pestle.

Thermal isomerization from fulleroids 2 and 3 into methanofullerene 4

(5,6)-Open fulleroids are reported to thermally rearrange to (6,6)-closed methanofullerenes.[6] Thus, we have studied the thermal isomerization from fulleroids **2** and **3** into methanofullerene **4**. Since it was quite difficult to separate **2**,**3**, and **4** and to obtain fulleroids **2** and **3** in a pure form, as described above, samples including mainly fulleroids **2** and **3** along with a slight amount of **4** were employed. A solution of fulleroids **2** and **3** in 1,1,2,2-tetrachloroethane-d_2, protected from light, was heated in an NMR tube at 120 °C. With the progress of time, **2** and **3** gradually decreased, whereas **4** increased, though the isomerization was extremely slow. The concentrations of **2** and **3** ($[\mathbf{2}]_t$, $[\mathbf{3}]_t$) were determined based on the integral ratio of ^{1}H NMR spectra, and the values ($([\mathbf{2}]_t + [\mathbf{3}]_t)/([\mathbf{2}]_0 + [\mathbf{3}]_0)$) were plotted against time (Fig. 3). The isomerization could be analyzed by first-order kinetics as follows:

$$-\ln\{([\mathbf{2}]_t + [\mathbf{3}]_t)/([\mathbf{2}]_0 + [\mathbf{3}]_0)\} = kt \qquad (3)$$

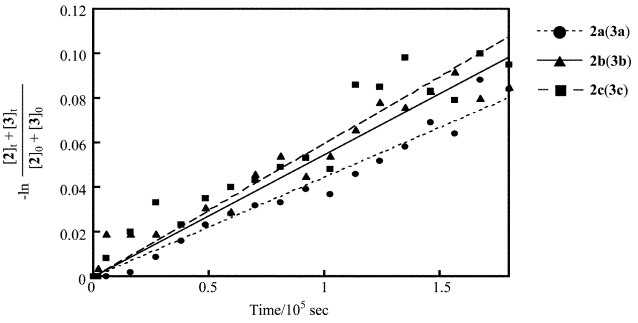


Fig. 3 Kinetics of thermal isomerization of **2a(3a)**, **2b(3b)** and **2c(3c)** at 120 °C in the absence of light.

Similar kinetic behavior has been reported for related fulleroids in the literature.[7] The first-order rate constants *k* for isomerization of **2a(3a)**, **2b(3b)**, and **2c(3c)** were 4.5 × 10^{-7}, 5.5 × 10^{-7}, and 6.0 × 10^{-7} s^{-1}, respectively. It seems that the difference of substituents on the benzene ring does not significantly affect the rate constants for the thermal isomerization, though the rate constants may increase slightly with the increasing electron-withdrawing property of substituents. The half-lives for isomerization of **2** and **3** are approximately 10 d under these conditions, and are consistent with a process in which the formation of **4** in the thermal reaction of diazoketones with [60]fullerene is primarily from **2** and **3**.

Photoisomerization from fulleroids 2 and 3 into methanofullerene 4

Fulleroids with a (5,6)-open structure are also known to photochemically isomerize into methanofullerenes with a (6,6)-closed structure.[7] Thus, the photoisomerization of fulleroids **2** and **3** into methanofullerenes **4** was also investigated.

A solution of fulleroids **2** and **3** in $CDCl_3$–CS_2 (1 : 1) was exposed to ambient light at room temperature. The amounts of **2** and **3** were monitored by ^{1}H NMR spectra, in a manner similar to that for thermal isomerization. The photoisomerization was also extremely slow, but it could be analyzed by first-order kinetics (Fig. 4). The first-order rate constants *k* for isomerization of **2a(3a)**, **2b(3b)**, and **2c(3c)** were 2.6 × 10^{-7}, 3.7 × 10^{-7}, and 4.4 × 10^{-7} s^{-1}, respectively. The rate constants of photoisomerization seem to slightly increase with an increase in the electron-withdrawing property of substituents, as in the case of the thermal isomerization.

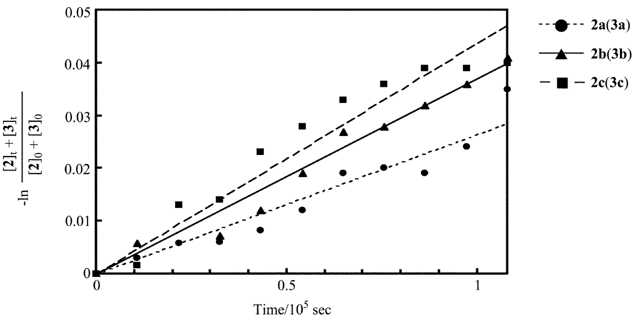


Fig. 4 Kinetics of photoisomerization of **2a(3a)**, **2b(3b)** and **2c(3c)** at room temperature under ambient light.

Summary

The reactions of **1a**–**c** with [60]fullerene were investigated in solution (ODCB) at 25 °C or in the solid-state. Under all the conditions examined, fulleroid **2** was obtained as a major product along with a slight amount of fulleroid **3** and methanofullerene **4**, while the reaction of **1b** with [60]fullerene at 100–150 °C was reported to give methanofullerene **4b** and dihydrofuran-fused fullerene derivative without the formation of fulleroid **2b** or **3b** in the literature.[9] The solid-state reactions considerably enhanced the reaction efficiency without affecting the selectivity. The thermal isomerization and photoisomerization from fulleroids **2** and **3** into methanofullerene **4** were relatively slow, almost independent of substituents under the conditions examined.

Experimental

General

NMR spectra were recorded on a JEOL α-500 or a JOEL AL-300 FT NMR spectrometer with tetramethylsilane as an internal standard in $CDCl_3$ at room temperature unless otherwise noted. APCI Mass spectra were taken by a Shimadzu LCMS-QP8000α mass spectrometer. Absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. GPC was performed with a JAI LC-918 R/U recycling preparative HPLC using JAIGEL-1H and 2H columns (solvent: $CHCl_3$) and a JAI LC-908 recycling preparative HPLC using JAIGEL-1H and 2H columns (solvent: toluene). The AM1 calculation was performed by CS Chem 3D Pro Ver 5.0 (Cambridge Soft Corporation). *o*-Dichlorobenzene (ODCB) was special grade reagents. Other materials and reagents were commercially available and used without further purification.

Preparation of diazomethane solution[10]

Diazomethane is especially toxic and prone to cause development of specific sensitivity. Therefore, use of glass apparatus with ground joints and sharp surfaces was avoided. Additionally, silicon grease was spread on connection parts.

A 100-ml three-necked flask was fitted with a Liebig condenser set for distillation and with a 200-ml long-stem dropping funnel. The condenser was connected by means of an adapter to a 500-ml round-bottom flask. The second hole of the adapter was fitted with a glass tube through a Teflon-tube connector. The outlet of the glass tube passed below the surface of ether (200 ml) in a 300-ml Erlenmeyer flask.

A mixture of carbitol (monoethyl ether of diethylene glycol, 35.6 g, 0.30 mol) in ether (10 ml) and potassium hydroxide (6.0 g, 0.11 mol) in water (10 ml) was heated in the three-necked flask at 75 °C with stirring by a Teflon-coated magnetic stirring bar. Then, *p*-tolylsulfonylmethylnitrosamide (21.4 g) in ether

(100 ml) was added from the dropping funnel over 30 min. As soon as all the nitrosamide solution was added, additional ether (50 ml) was placed in the dropping funnel and added at the previous rate until the distillate was colorless. As a consequence of this procedure, diazomethane solution (*ca.* 300 ml) was obtained in the round-bottom flask (*ca.* 100 ml) and the Erlenmeyer flask (*ca.* 200 ml). The yield in this procedure was estimated as 50% (0.050 mol), while the yield in the literature was 67%.[10]

Preparation of 2-diazo-1-(4-methoxyphenyl)ethanone (1a),[11b] 2-diazo-1-phenylethanone (1b),[11] and 2-diazo-1-(4-bromophenyl)ethanone (1c)[11b]

A mixture of the diazomethane solution (*ca.* 300 ml, 0.050 mol) prepared above and triethylamine (0.032 mol) was stirred on an ice-water bath at 0 °C for 5 min. *p*-Substituted benzoyl chloride **5** (0.026 mol: 4-methoxybenzoyl chloride (**5a**), 4.36 g; benzoyl chloride (**5b**), 3.60 g; 4-bromobenzoyl chloride (**5c**), 5.62 g) in diethyl ether (5 ml) was added from a 10-ml dropping funnel over 5 min. The mixture was stirred for additional 2 h at 0 °C and overnight at room temperature. After the triethylamine hydrochloride formed was removed by filtration, the solvent was evaporated under reduced pressure. Purification of the residue by column chromatography (silica gel, ethyl acetate–hexane) gave diazoketone **1** (**1a** (1.41 g, 31%), **1b** (0.67 g, 17%), **1c** (1.63 g, 28%)).

1a: δ_H (500 MHz; $CDCl_3$) 7.74 (2 H, d, *J* 9), 6.93 (2 H, t, *J* 10), 5.84 (1 H, s), 3.86 (3 H, s).

1b: δ_H (500 MHz; $CDCl_3$) 7.76 (2 H, d, *J* 5.0), 7.55 (1 H, t, *J* 7.5), 7.47 (2 H, t, *J* 10.0), 5.90 (1 H, s).

1c: δ_H (500 MHz; $CDCl_3$) 7.61 (4 H, m), 5.87 (1 H, s).

Procedure for reactions of [60]fullerene with diazoketones 1a–c in ODCB

[60]Fullerene (216 mg, 0.30 mmol) in ODCB (15 ml) was added to four test tubes (volume: 20 ml) with caps. These solutions were ultrasonicated for 2 h and stirred on an oil bath at 25 °C for overnight. After the temperature was stabilized, diazoketone **1** (0.033 mmol: **1a**, 58 mg; **1b**, 48 mg; **1c**, 74 mg) was added to each of these test tubes. These mixtures were stirred for 2 weeks. Purification of the products in ODCB by column chromatography (silica gel, toluene–hexane) and GPC (chloroform or toluene), if necessary, and the subsequent freeze-drying (benzene) gave mixture of **2**–**4** (**2a**–**4a**: 40 mg (15%); **2b**–**4b**: 12 mg (5%); **2c**–**4c**: 9 mg (1%)).

^1H NMR spectral data ($CDCl_3$–CS_2 (1 : 1), 300 MHz) of mixture **2**–**4** are summarized in Table 2.

Mixture of **2a**–**4a**: APCI-Mass *m*/*z* 868 (M^-), 720 (C_{60}^-).

Mixture of **2b**–**4b**: APCI-Mass *m*/*z* 838 (M^-), 720 (C_{60}^-).

Mixture of **2c**–**4c**: APCI-Mass *m*/*z* 917 (M^-), 720 (C_{60}^-).

Procedure for solid-state reactions using agate mortar and pestle (method A)

[60]Fullerene (144 mg, 0.20 mmol) was ground by agate mortar and pestle for 1 h in advance. To the [60]fullerene was added diazoketone **1** (0.22 mmol; **1a**, 39 mg; **1b**, 32 mg; **1c**, 50 mg) in diethyl ether (5 ml) dropwise with grinding for 5 min. After the mixture was ground for additional 30 min, the reaction mixture was obtained.

Procedure for solid-state reactions using high-speed vibration milling (HSVM) (method B)

The HSVM apparatus, which was fabricated by Nippon Gerotor Co., Ltd., was used throughout this study by combining a capsule and milling balls (diameter 1 mm) made of stainless steel (SUS304).

[60]Fullerene (144 mg, 0.20 mmol) was ground by agate mortar and pestle for 1 h in advance. Diazoketone **1** (0.22 mmol: **1a**, 39 mg; **1b**, 32 mg; **1c**, 50 mg) was also ground by another agate mortar and pestle for 10 min in advance. The mixture and the 50 stainless balls were placed into a capsule, which was capped tightly. The capsule was fixed to the HSVM apparatus so that the capsule was shaken along its long axis horizontally with a slight fluctuation (rotating motion) for 1 h at 3000 rpm. The product formed was purified as above.

Kinetic studies of thermal isomerization from fulleroids 2 and 3 into methanofullerene 4 (general procedure)

A 5-mm NMR tube, wrapped with aluminum foil, was charged with the samples (8.7 mg, 0.010 mmol) including mainly fulleroids **2a** and **3a** along with a small amount of **4a** and 1,4-dimethoxybenzene (1.4 mg, 0.010 mmol) as reference dissolved in 1,1,2,2-tetrachloroethane-d_2 (0.75 mL). The NMR tube was allowed to stand on an oil bath kept at 120 °C. At intervals, the tube was cooled to room temperature and the NMR spectrum was measured. The NMR tube was heated for 50 h in total.

Kinetic studies of photoisomerization from fulleroids 2 and 3 into methanofullerene 4 (general procedure)

A 5-mm NMR tube, wrapped with aluminum foil, was charged with the samples (8.7 mg, 0.010 mmol) including mainly fulleroids **2a** and **3a** along with a small amount of **4a** and 1,4-dimethoxybenzene (1.4 mg, 0.010 mmol) as reference dissolved in $CDCl_3$–CS_2 (1 : 1) (0.75 mL). The NMR tube was exposed to ambient light at room temperature. At intervals, the NMR spectrum was measured. The NMR tube was exposed to ambient light for 30 h in total.

Acknowledgements

This work was financially supported by grants from the Ministry of Education, Science, Sports, and Culture, Japan. The authors are grateful to Mr. Yuji Kawano of Nippon Gerotor Co., Ltd. for the fabrication of the HSVM apparatus.

References

1 (*a*) A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994; (*b*) F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157; (*c*) R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; (*d*) A. Hirsch, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1138; (*e*) F. Diederich, L. Isaacs and D. Philp, *Chem. Soc. Rev.*, 1994, **23**, 243; (*f*) W. Sliwa, *Fullerene Sci. Technol.*, 1995, **3**, 243; (*g*) A. Hirsch, *Synthesis*, 1995, **8**, 895; (*h*) F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317.

2 (*a*) C. Bingel, *Chem. Ber.*, 1993, **126**, 1957; (*b*) M. Tsuda, T. Ishida, T. Nogami, S. Kurono and M. Ohashi, *Tetrahedron Lett.*, 1993, **34**, 6911; (*c*) H. Tokuyama, M. Nakamura and E. Nakamura, *Tetrahedron Lett.*, 1993, **34**, 7429; (*d*) L. Isaacs and F. Diederich, *Helv. Chim. Acta*, 1993, **76**, 2454; (*e*) Y.-Z. An, Y. Rubin, C. Schaller and S. W. McElvany, *J. Org. Chem.*, 1994, **59**, 2927; (*f*) H. L. Anderson, R. Faust, Y. Rubin and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1366; (*g*) A. Vasella, P. Uhlmann, C. A. A. Waldraff, F. Diederich and C. Thilgen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1388.

3 T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7301.

4 (*a*) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens and R. C. King, *J. Am. Chem. Soc.*, 1993, **115**, 5829; (*b*) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt and R. C. King, *J. Am. Chem. Soc.*, 1995, **117**, 5492.

5 F. Wudl, *J. Mater. Chem.*, 2002, **12**, 1959.

6 (*a*) L. Isaacs, A. Wehrsig and F. Diederich, *Helv. Chim. Acta*, 1993, **76**, 1231; (*b*) M. Prato, V. Lucchini, M. Maggini, E. Stimpfl, G. Scorrano, M. Eiermann, T. Suzuki and F. Wudl, *J. Am. Chem. Soc.*, 1993, **115**, 8479; (*c*) F. Diederich, L. Isaacs and D. Philp, *J. Chem. Soc., Perkin Trans. 2*, 1994, 391; (*d*) A. Skiebe and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1994, 335; (*e*) J. Osterodt, M. Nieger, P.-M. Windscheif and F. Vogtle, *Chem. Ber.*, 1993, **126**, 2331.

7 (*a*) R. A. J. Janssen, J. C. Hummelen and F. Wudl, *J. Am. Chem. Soc.*, 1995, **117**, 544; (*b*) Z. Li and P. B. Shevlin, *J. Am. Chem. Soc.*, 1997, **119**, 1149; (*c*) M. H. Hall, H. Lu and P. B. Shevlin, *J. Am.*

Chem. Soc., 2001, **123**, 1349; (*d*) R. González, J. C. Hummelen and F. Wudl, *J. Org. Chem.*, 1995, **60**, 2618.
8 (*a*) M. Eiermann, F. Wudl, M. Prato and M. Maggini, *J. Am. Chem. Soc.*, 1994, **116**, 8364; (*b*) F. Arias, L. Echegoyen, S. R. Wilson, Q. Lu and Q. Lu, *J. Am. Chem. Soc.*, 1995, **117**, 1422.
9 H. J. Bestmann, C. Moll and C. Bingel, *SYNLETT*, 1996, 729.
10 Th. J. de Boer and H. J. Backer, *Org. Synth.*, 1962, **Coll. Vol. 4**, 250.
11 (*a*) J. N. Bridson and J. Hooz, *Org. Synth.*, 1988, **Coll. Vol. 6**, 386; (*b*) M. Regitz, F. Menz and J. Rüter, *Tetrahedron Lett.*, 1967, **8**, 739.
12 (*a*) R. C. Haddon, *Nature*, 1995, **378**, 249; (*b*) M. Prato, T. Suzuki, F. Wudl, V. Lucchini and M. Maggini, *J. Am. Chem. Soc.*, 1993, **115**, 7876.
13 Y. Wang, J. Cao, D. I. Schuster and S. R. Wilson, *Tetrahedron Lett.*, 1995, **36**, 6843.
14 G. Schick and A. Hirsch, *Tetrahedron*, 1998, **54**, 4283.
15 H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.
16 For review, see: K. Komatsu, K. Fujiwara, T. Tanaka and Y. Murata, *Carbon*, 2000, **38**, 1529 and references cited therein.