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Diastereoselective syntheses and oxygenation of silyl fulleroids

Yoshio Kabe [a,*], Houjin Hachiya [a], Tomohisa Saito [a], Daisuke Shimizu [a], Masakatsu Ishiwata [a], Kazuharu Suzuki [b], Yuko Yakushigawa [b], Wataru Ando [b]

[a] Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka 259-1293, Japan
[b] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

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ABSTRACT

The addition of silyl diazomethane (**1a–d**) to fullerene C_{60} at room temperature provided the mono-adducts, the bis- and tris-adducts of silyl fulleroid (**3a–d**) in moderate yields. The structures of the silyl fulleroids were characterized by mass spectroscopy, as well as ^1H and ^{13}C NMR. The gated ^1H NMR and ^{13}C–^1H COLOC analyses of **3a–d** showed a correlation between the methine proton resonances and three fullerene carbons. These observations, as well as the ^1H NMR chemical shifts of the methine protons, suggest a remarkable diastereoselectivity, with the silyl groups located above a five-membered ring. Two transition states of the thermal nitrogen-extrusion of pyrazoline intermediate (**2a**) were theoretically obtained, the structures of which disclosed that the diastereoselectivity is a consequence of minimization of the repulsive interaction between the silyl groups and the N_2 moiety. The bridgehead C=C double bond of the silyl fulleroid is thought to be reactive by POAV analyses. The silyl fulleroids (**3a**,**b**) were found to react with singlet oxygen to afford the silyl enol ether (**9a**,**b**) via 1,3-silyl migration of a diketone (**8a**,**b**). This is the first example of $^1O_2$ oxygenation of fulleroids.

1. Introduction

Among the various fullerene derivatives, fulleroids and their nitrogen analog (azafulleroid) with [5,6] C_{60} open structures have attracted great interest in the synthesis of open-cage fullerenes for application as encapsulated and hetero fullerenes [1,2]. The addition of diazo or azide compounds to C_{60} has been the only known route to the formation of fulleroid or azafulleroid [3,4]. Concerted nitrogen-extrusion of the [6,6] pyrazoline and triazoline intermediate (**I**) (X = CR_2 or NR, as shown in Scheme 1) formed initially takes place to rearrange the [5,6] open fulleroid (**III**) via a retro [2+2+2] cycloreaction of an unknown [5,6] closed methanofullerene (**II**) [5]. Subsequent oxidative C=C bond cleavage of the azafulleroids (**IV**; X = NR) by singlet oxygen ($^1O_2$) is the key step in opening a hole in the fullerene surface. Another approach is the bisfulleroid route, which involves photochemical [4+4] cycloaddition of cyclohexadine derivatives of C_{60} (**V**; E = N, CR_1) followed by a retro [2+2+2] cycloreaction (**VI**). Oxygenation of bisfulleroids (**VII**) also affords an open-cage fullerene (**VIII**) having larger rings on its surface.

Using the two essentially identical reaction routes, several derivatives of open-cage fullerenes have been prepared [1,2]. However, to date no information has been reported regarding the $^1O_2$ oxygenation of fulleroids (**III**; X = CR_2) and their derivatives. Herein, the reaction of silyl-substituted diazomethane with C_{60} is reported to proceed in a diastereoselective fashion to yield silyl fulleroids, which undergo $^1O_2$ oxygenation with 1,3-silyl group migration to afford the silyl enol ether derivatives of C_{60}. In order to explore the diastereoselectivity of the first step, the mechanism of the decomposition of the 1,3-dipolar adduct of silyl diazomethane was theoretically investigated. The reactivity of the bridgehead double bond of the silyl fulleroid and the related fullerene was estimated by π-orbital axis vector (POAV) analysis.

2. Results and discussion

2.1. Diastereoselective formation of silyl fulleroids

The mono-silyl diazomethane (**1a–d**) was slowly added to a toluene solution of C_{60} at room or reflux temperature, and the products were separated by gel permeation chromatography (GPC). The mono-adducts (**3a–d**) were isolated in 19–41% yield as well as the bis- and tris-adducts (12–29% and 8–24% yield), and were analyzed by FAB or TOF mass spectroscopy, as shown in Scheme 2 and Table 1. The ^1H NMR chemical shifts of the methine proton of **3a–d** can be used as a sensitive NMR probe for the segregated ring currents of the fullerene core. For **3a–d**, the methine protons appeared upfield (2.47–3.43 ppm) of **1a–d**, typical for a location above the six-membered ring of a bridged fullerene subunit. In the ^1H-decoupled ^{13}C NMR spectra of **3a–d**, 32 resonances were assigned to the C_{60} skeleton. Of the 32, 28 signals have a relative intensity of 2 and 4 signals have an intensity of 1, indicating C_S symmetry. Moreover, in the

* Corresponding author. Tel./fax: +81 0463 59 4111.
E-mail address: kabe@kanagawa-u.ac.jp (Y. Kabe).

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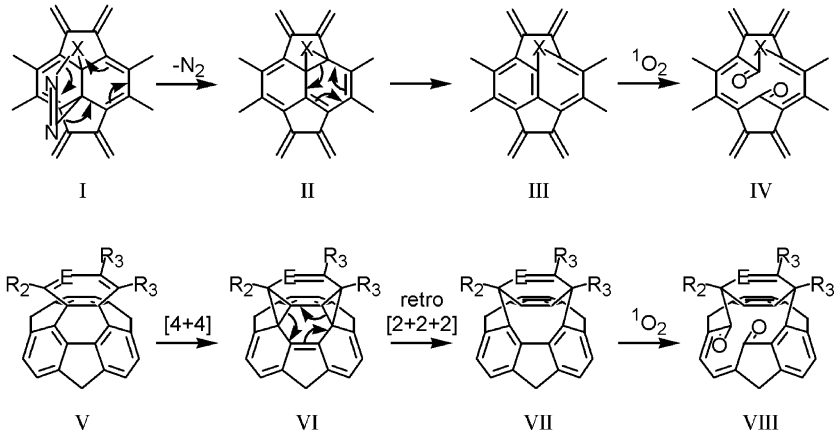
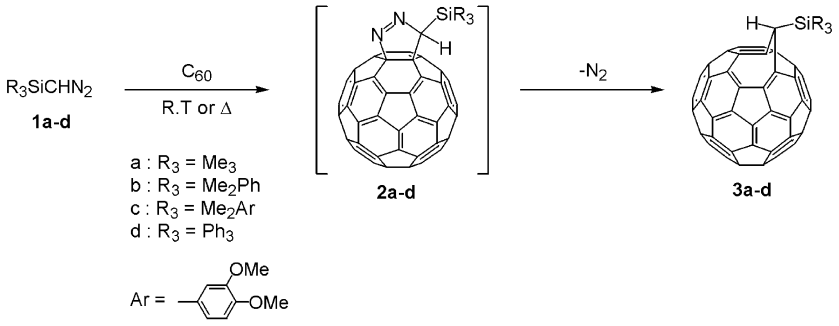


Scheme 1.



Scheme 2.

Table 1
Yields of monosilyldiazomethane adducts.

Reactant (R_3SiCHN_2)	Yields (%) and ion peaks		
	Mono-adducts **3**	Bis-adducts[a]	Tris-adducts[b]
1a: $R_3 = Me_3$	34, (M^+ = 806)	24, (M^+ = 892)	22, (M^+ = 978)
1b: $R_3 = Me_2Ph$	41, (M^+ = 868)	29, (M^+ = 1016)	8, (M^+ - H = 1164)
1c: $R_3 = Me_2Ar$[c]	41, (M^+ = 929)	29, (M^+ = 1138)	18, (M^+ = 1348)
1d: $R_3 = Ph_3$	19 (17.4)[d], (M^+ = 992)	12, (M^+ = 1265)	24, (M^+ = 1537)

[a] Bis-adducts: $C_{60}(R_3SiCH)_2$.
[b] Tris-sadduts: $C_{60}(R_3SiCH)_3$.
[c] Ar: 3,4-$(OMe)_2C_6H_4$.
[d] 1:2 mixture of **7** and **3d**.

gated ^{1}H-coupled ^{13}C NMR spectra of **3a–d**, the three sets of fullerene carbons at 136.7–137.0 ppm, 138.2–140.0 ppm and 143.7–143.8 ppm are split into doublets ($^{2,3}J_{C-H}$ = 5.3–7.4 Hz) by the methine protons. ^{13}C–^{1}H COLOC analysis also showed a correlation between the methine proton resonances and the same three fullerenes resonances. Typical spectra (**3c**) are shown in Figs. 1 and 2, and Table 2. The ^{13}C–^{1}H long range coupling supports the conclusion that **3a–d** have [5,6] open fulleroid structures with silyl groups located above a five-membered ring, as shown in Scheme 2. Recently, it was reported that monoalkylated [3k,5d] and alkylphenylated diazoalkanes [6b,c,e] react with C_{60} with remarkable regio- and diastereoselectivity to yield stable fulleroids with the bulkier substituent located above a five-membered ring.

On the other hand, bis(trimethylsilyl) diazomethane (**4e**) did not react with C_{60} under similar conditions, even under reflux and photolysis, as shown in Scheme 3. Trimethylsilyl pentamethyldisilyl diazomethane (**4f**) reacts with C_{60} under photolysis in toluene to afford **5** in 56% yield with recovered C_{60}. The structure of **5** was elucidated by reported spectral data and X-ray analysis [7f]. The formation of **5** is thought to be the result of the dimerization of silene, which was formed by trimehylsilyl migration from a silicon atom to the carbon center shown in Scheme 3 [7]. Thus, bulky bissilyl diazomethane seems to inhibit the [2+3] cycloaddition of diazomethane with C_{60}, and silene is not added to C_{60} because of its bulkiness and electrophilicity.

Phenyltrimethylsilyl diazomethane (**4g**) combined with C_{60} under reflux yielded the mono-adduct (**6**) in 46% yield. In the ^{13}C NMR spectrum of **6**, two quaternary carbons appear in the aliphatic region. The higher field resonance at 48.0 ppm is assigned to the methano-bridged carbon, slightly lower than those of **3a-d** (38.0–40.7 ppm). The lower field resonance at 78.1 ppm is assigned to the bridgehead carbon supporting the [6,6] closed methanofullerene structure. These chemical shifts are very close to the reported values (43.1 ppm and 75.6 ppm) of [6,6] closed methanofullere derived from *p*-methoxyphenyldiazomethane combined with C_{60} [3f]. Whereas various reagent produce exclusively the [6,6] closed isomers, diazoalkane addition is the only known route to the formation of [5,6] open fulleroids. Most [5,6] fulleroids are quite labile, and therefore thermally, photochemically and electrochemically isomerize to the [6,6] open methanofullerene [6]. The formation of **6** is postulated to involve either thermal conversion of [5,6] fulleroid or silyl carbene addition. In fact, the reaction of mono-silyldiazomethane **1d** with C_{60}, at higher temperature resulted in the formation of the [6,6] closed isomer (**7**) in addition to the [5,6] open fulleroid (**3d**), in 17.4% yield, as 1:2 mixture.

2.2. Theoretical studies on thermal nitrogen-extrusion of [6,6] closed silylpyrazoline

In order to elucidate the origin of the diastereoselectivity in the addition of silyldiazomethanes to C_{60}, the mechanism of N_2

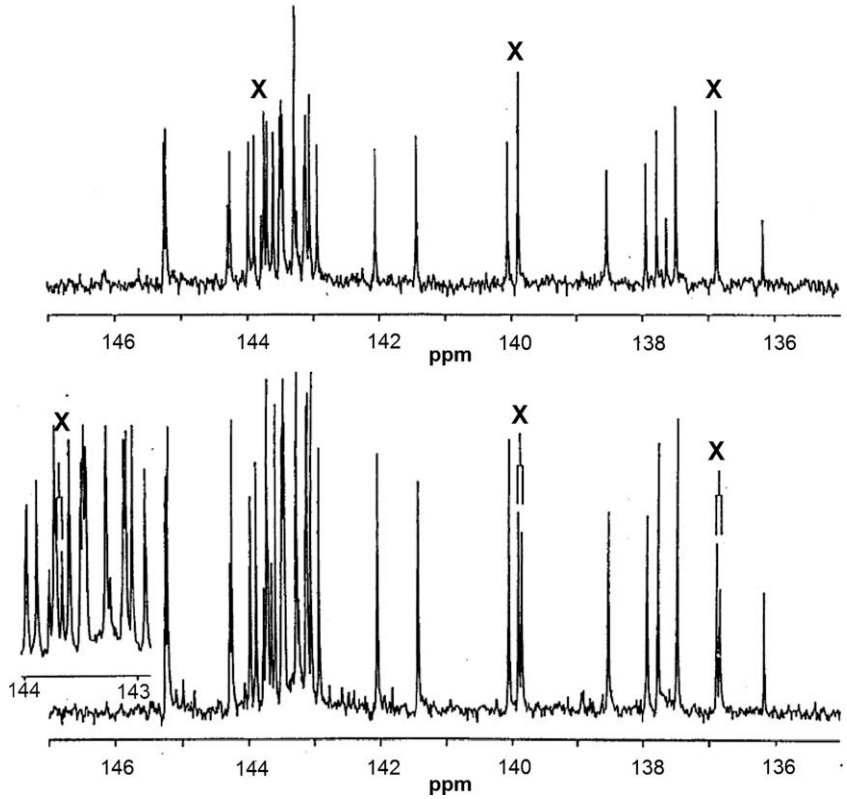


Fig. 1. ^{13}C NMR (top) and gated decoupled ^{13}C NMR (bottom) of the fullerene region of **3c**. X denotes ^{13}C–^{1}H long couplings.

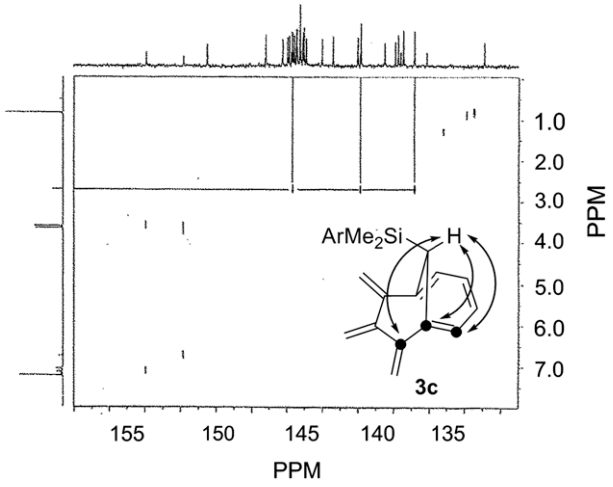


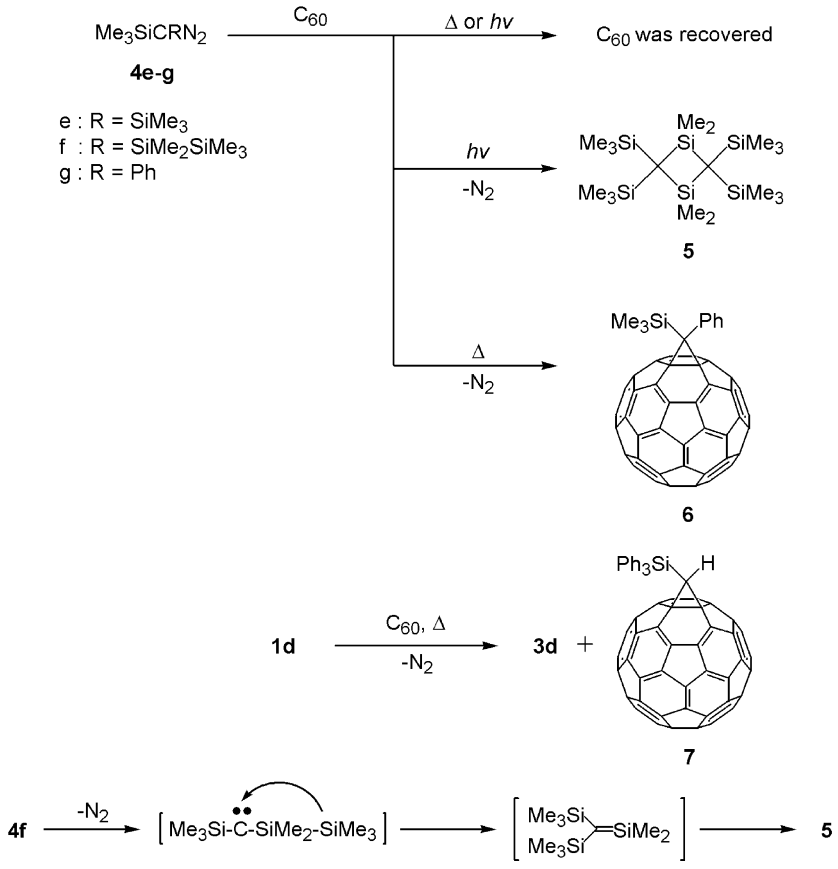
Fig. 2. ^{13}C–^{1}H COLOC NMR spectrum of **3c**.

Table 2
Selected ^{1}H and ^{13}C NMR spectral data for **3a–d**.

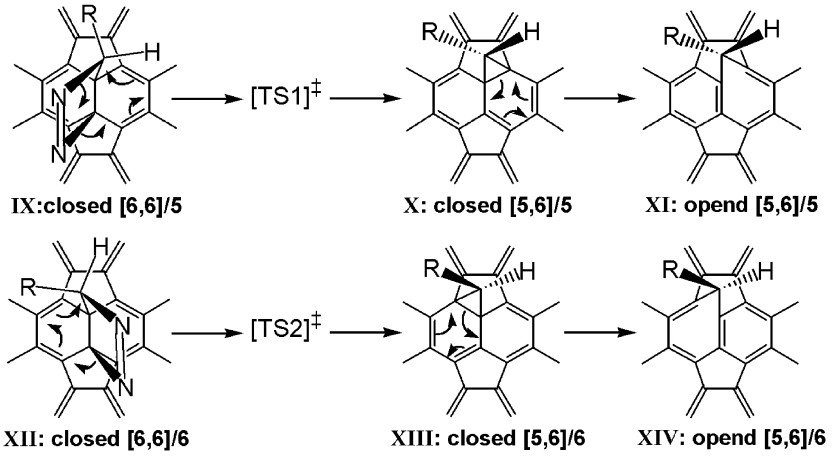
	^{1}H NMR δ/ppm	^{13}C NMR δ/ppm	
	H at bridging C	Bridging C ($^{1}J_{C-H}$, Hz)	Fullerene carbons ($^{2,3}J_{C-H}$, Hz)
3a	2.47	40.5 (126.5)	136.7 (5.9), 140.0 (6.1), 143.7 (6.0)
3b	2.69	40.3 (125.8)	136.7 (6.3), 139.5 (6.0), 143.7 (6.3)
3c	2.69	40.7 (125.8)	136.7 (6.3), 139.9 (6.4), 143.7 (5.3)
3d	3.43	38.0 (127.3)	137.1 (6.4), 139.3 (6.4), 143.7 (6.1)

extrusion from the silylpyrazoline intermediate was studied by ab initio Hartree–Fock methods. For the silylpyrazoline, two possible conformers exist, the closed [6,6]/5 (**IX**) and closed [6,6]/6 (**XII**) conformers, as shown in Scheme 4. In the closed [6,6]/5 conformer (**IX**), the silyl group (R = SiR'_3) faces the pentagonal ring, whereas in the closed [5,6]/6 conformer (**XII**) the silyl group (R = SiR'_3) faces the hexagonal ring. Schemes 4 and 5 show the concerted and stepwise nitrogen-extrusion mechanisms, respectively. Because of the high energy of the stepwise mechanism [5c] and the same stereochemical consequence on both mechanisms [5d], the stepwise mechanism was neglected in the remainder of arguments. Thermal nitrogen-extrusion of the two conformers of pyrazoline (**IX** and **XII**) takes place leading to the corresponding opened [5,6]/5 and [5,6]/6 fulleroid (**XI** and **XIV**) via the closed [5,6]/5 and [5,6]/6 methanofullerenes (**X** and **XIII**), respectively. Experimentally, only the opened [5,6]/5 fulleroid (**XI**) was isolated, not the [5,6]/6 fulleroid (**XIV**). During the formation of the fulleroids, the silyl groups (R = SiR'_3) have to move toward the N_2 moieties, or move from it, no matter which mechanism, concerted or stepwise, is considered.

The transition state (TSs) of two reaction pathways for trimethylsilyl pyrazoline (**2a**, R = $SiMe_3$) were analyzed using RHF/STO-3G, as shown in Fig. 3. In TS1, the silyl groups move away from the N_2 moiety. For TS2, the silyl groups move toward the N_2 moiety. The two TSs corresponding to the thermal extrusion of nitrogen from pyrazoline were located at the RHF/STO-3G level. Vibrational analyses verified that both are first-order saddle points corresponding to the extrusion of N_2 with imaginary frequencies of -1164 and -1046 cm^{-1} for TS1 and TS2, respectively. RHF/STO-3G calculation favors TS1 over TS2 by more than 6.9 kcal mol^{-1}, in agreement with experimental results. To confirm that TS1 and TS2 are connected to the closed [6,6] pyrazoline and the opened [5,6] fulleroids, the intrinsic reaction coordinates (IRCs) starting from these TSs were constructed, as shown in Fig. 4. In fact, it was found that the two TSs are connected to the closed [6,6] pyrazoline. Interestingly, the two TSs are also connected the closed [5,6] methanofullerenes, which are located in very shallow minima. In all cases, the most favorable pathway is for the sterically demanding silyl group to



Scheme 3.

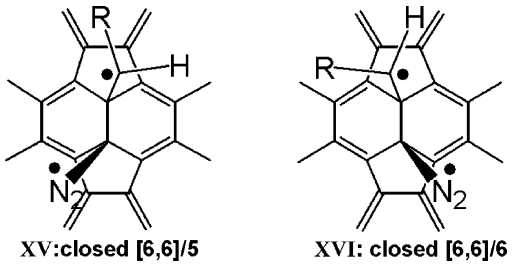


Scheme 4.

move away from the N_2 moiety. For the more bulky triphenylsilylpyrazoline **2d**, the energy difference between the two TSs increased to 9.4 kcal mol^{-1}, with imaginary frequencies of −1169 and −1032 cm^{-1} for TS1 and TS2, respectively. Single-point calculations using density functional theory B3LYP/6-31G**//HF/STO-3G were also carried out. The calculations lowered the energy differences between TS1 and TS2 with 2.1 and 3.0 kcal mol^{-1} for **2a** and **2d**, respectively. For comparison, for the carbon analog **IX** and **XII** (R = CMe_3), RHF/STO-3G calculations predicted a 9.7 kcal mol^{-1} energy difference, with imaginary frequencies of −1100 and −815 cm^{-1} for TS1 and TS2, respectively. Close inspection of TS1 and TS2 shown in Fig. 3 shows that the pronounced diastereoselectivity is a consequence of the minimization of the repulsive interaction between the silyl groups and the N_2 moiety, which produce the fulleroid with the silyl group located above a five-membered ring.

2.3. POAV analyses of silyl fulleroids

As shown in Scheme 1, azafulleroid (**III**; X = NR) and bisfulleroid (**VII**; E = N, CR) undergo regioselective oxidative cleavage of the bridgehead double bond by singlet oxygen. However, there is no information regarding fulleroids. The calculated structure of aza-



XV:closed [6,6]/5 XVI: closed [6,6]/6

Scheme 5.

fulleroid is known to have a shorter bridgehead bond length (1–9 and 5–6 bonds) and more pyramidalization than the parent fulleroid, violating Bredt's rule by POAV analyses [8]. Actually, the pyramidalization angles of azafulleroid $C_{60}NH$ (C1, C5 (8.1°) and C6, C9 (10.2°)) is reported to be greater than the parent fulleroid (C1, C5 (7.6°) and C6, C9 (9.5°)), but in all cases are reduced from the values that are implicit in the parent C_{60} molecules (11.6°). Whereas $^1O_2$ oxygenations of mixture of diphenyl-substituted fulleroid and methanofullerene were carried out, the ^1H NMR spectrum of the fulleroid region (7.3–8.0 ppm) showed no change in comparison with the initial spectrum [9]. Thus, the fulleroid does not appear to show any evidence of reaction at the 1–9 and 5–6 bonds. However, introduction of a substituent at the bridged carbon is thought to make this the site more reactive under certain circumstance. So, POAV analyses of phenyl- and silyl-substituted fulleroids, as well as bisfulleroids, were carried out (Table 3). Inspection of Table 3, the pyramidalization angles of fulleroids at C6 and C9 and those of bisfulleroid at C6 and C7 are large values, while the values of fulleroids at C1 and C5 and those of bisfulleroids at C5 and C8 are small values. At least, within the values at C6 and C9, when changing from parent, phenyl and silyl fulleroids, the pyramidalization angles tend to increase. Thus the calculations on the silyl-substituted fulleroid predict the reactivity toward $^1O_2$ at the C1–C9 and C5–C6 bonds.

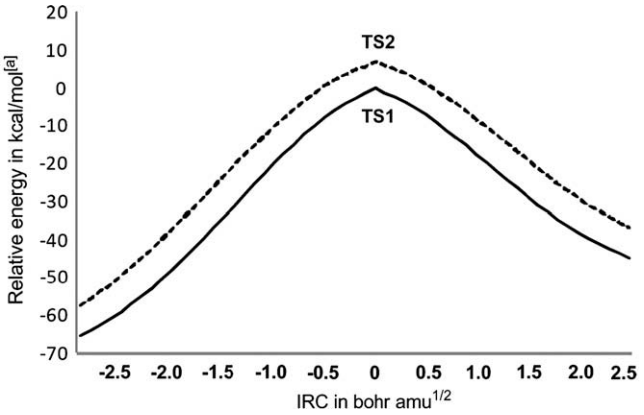


Fig. 4. IRC calculations of N_2 extrusion from the closed [6,6]/5 and [6,6]/6 pyrazolines. [a] Energies were estimated relative to TS1 as 0.0 kcal/mol.

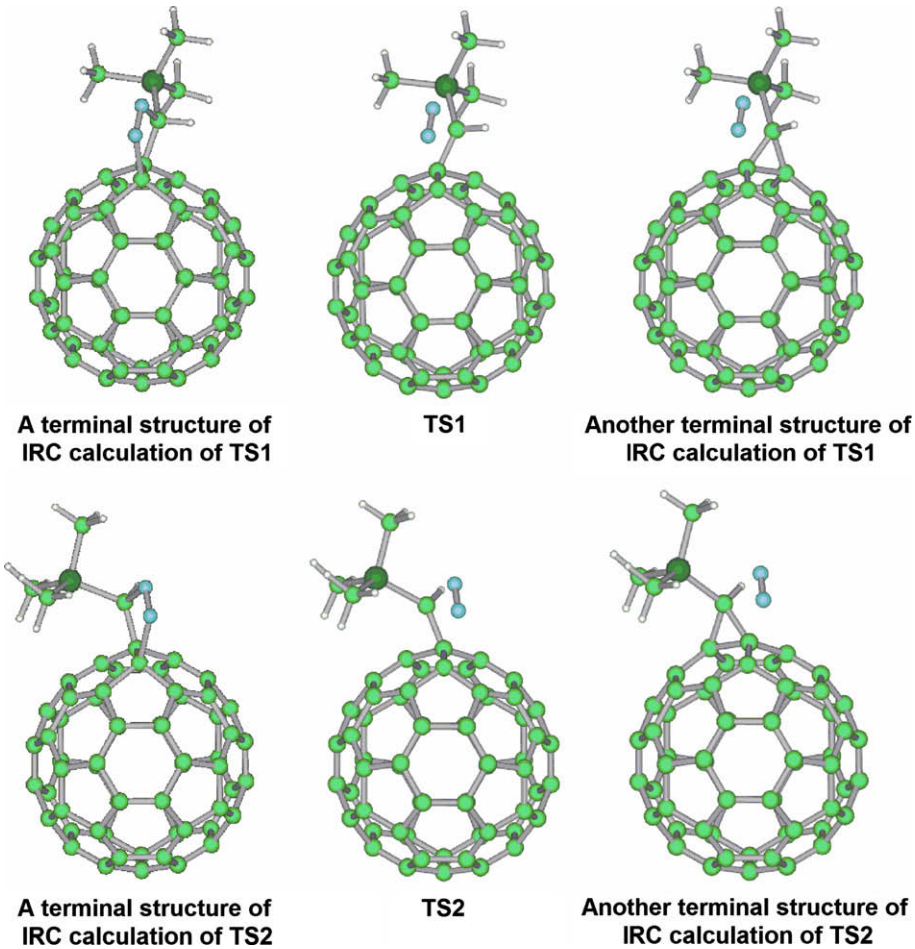


Fig. 3. Calculated (RHF/STO-3G) structures of TS1 and TS2 with terminal structures of IRC calculations.

Table 3
Calculated fulleroid pyramidalization angles (°).[a]

Fulleroid (left)[b]	C1, C5	C2, C4	C3	C6, C9	C7, C8
$R_1 = R_2 = H$	7.9	9.4	10.4	9.3	11.1
$R_1 = R_2 = Ph$	7.0	9.2	10.3	8.9	11.2
$R_1 = SiMe_3$, $R_2 = H$	7.7	9.4	10.2	9.4	11.0

Bisfulleroid (right)[b]	C1, C12	C2, C11	C3, C10	C4, C9	C5, C8	C6, C7
E = C, $R_3 = R_4 = H$	7.3	8.1	10.0	8.6	5.9	9.7
E = N, R_3 = Py, R_4 = Ph	7.1, 6.5	8.0, 8.0	9.9, 9.9	8.6, 8.3	5.7, 6.2	9.6, 9.5

[a] Geometries optimized using B3LYP/6-31G** basis set.
[b] See Fig. 5.

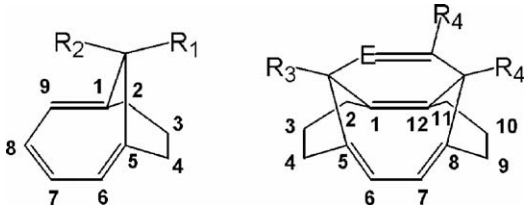


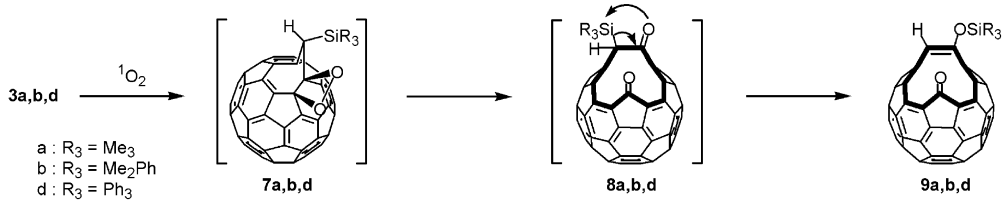
Fig. 5. Partial atomic numbering of fulleroid (left) and bisfulleroid (right).

2.4. $^1O_2$ oxygenation of silyl fulleroids

Based on the POAV analyses, $^1O_2$ oxygenation of **3a**, **3b** and **3d** were carried out. A solution of **3a**,**b** in *o*-dichlorobenzene was exposed to a halogen lamp (300 W) for 5 h under an oxygen stream. Although the reaction in *o*-dichlorobenzene at room temperature was sluggish, using CS_2 as a solvent at −60 °C resulted in a relatively clean reaction. The ^1H NMR spectrum of the reaction mixture of **3a** showed two new singlet at 0.57 and 5.87 ppm, in addition to those observed for **3a** at 0.60 and 2.57 ppm for the $SiMe_3$ and CH protons. Similarly, the ^1H NMR spectrum of the reaction mixture of **3b** showed three singlet at 0.84, 0.85 and 5.90 ppm, in addition to those observed of **3b** at 0.75 and 2.69 ppm for $SiMe_2$ with CH protons. In the case of **3b** the non equivalence of SiMe suggested C_1 symmetry of oxidation product. After GPC, **9a**,**b** were obtained in 15% and 12% yields, from **3a** and **3b**, respectively.

The product **9a**,**b** are proposed to be a silyl enol ether on the basis of spectroscopic characteristics, as shown in Scheme 6. The molecular ion peak at 831 ($[M+1]^+$) of **9a** and 901 ($[M+1]^+$) of **9b** were detected by MALDI-TOF mass spectroscopy, indicating that the product were formed by addition of O_2 to **3a** and **3b**. The ^1H NMR resonance of the CH protons was shifted to lower field (5.87 and 5.90 ppm) for **3a** and **3b**, assigned to the olefin protons. Due to the low solubility of **9a**, it was not possible to obtain the ^{13}C NMR spectrum. However, the ^{13}C NMR spectrum of **9b** displayed two signals at 199.7 ppm for carbonyl carbon and at 97.68 ppm for olefinic methine carbon, as shown in Fig. 6. Silyl enol ether derivatives of bisfulleroids were reported that ^{13}C NMR chemical shifts of enol methine carbons are 101.54 ppm [10]. In the fullerene carbon region of **9b**, 54 signals were observed, indicating that **9b** has C_1 symmetry. The IR spectra of **9a** and **9b** showed strong bands at 1733 cm^{-1} corresponding to a carbonyl group and a strong band at 1100 cm^{-1} corresponding to Si–O groups. Although, ^{13}C NMR characterization of **9a** was precluded, all data are in agreement with silyl enol ether structures of **9a** and **9b**. The [2+2] cycloaddition of **3a**,**b** with $^1O_2$ followed by symmetrical ring opening of **7a**,**b** is thought to occur to give the diketone derivative **8a**,**b**. Subsequent 1,3-silicon migration of **8b** affords the silyl enol ether derivatives of C_{60}. The 1,3-silicon migration is highly dependent upon the silicon atom substituent [11]. Oxygenation of **3d** in CS_2 at −60 °C proceeded similarly. Three assignable new peaks 5.81, 5.91 and 5.96 ppm in ^1H NMR spectra were observed. However, due to the instability of products, all attempts of isolation and characterization met with failure.

Theoretical calculations also support the 1,3-silyl migration. The optimized structures of the silyl enol ether **9a** and diketone **8a** calculated at B3LYP/6-31G level of theory, as shown in Fig. 7. The relative energy of diketone **9a** is calculated lower than that of **8a** by 21 kcal mol^{-1}. The NMR chemical shifts of **8a** and **9a** were also estimated by GIAO calculations (B3LYP/6-31G). The calculated



Scheme 6.

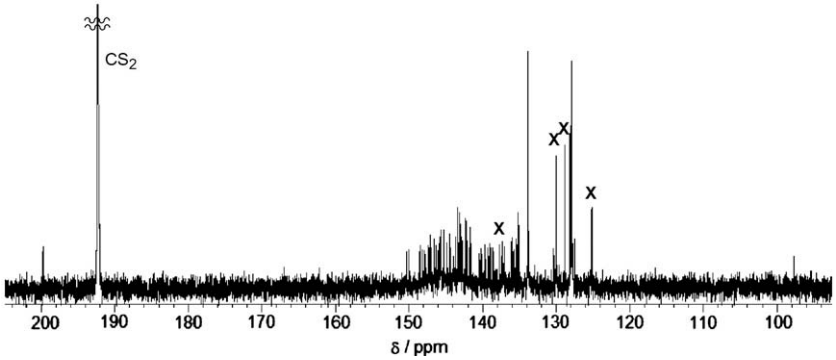


Fig. 6. ^{13}C NMR sp^2 carbon region of **9b** in CS_2: $CDCl_3$ solution. X denotes as toluene.

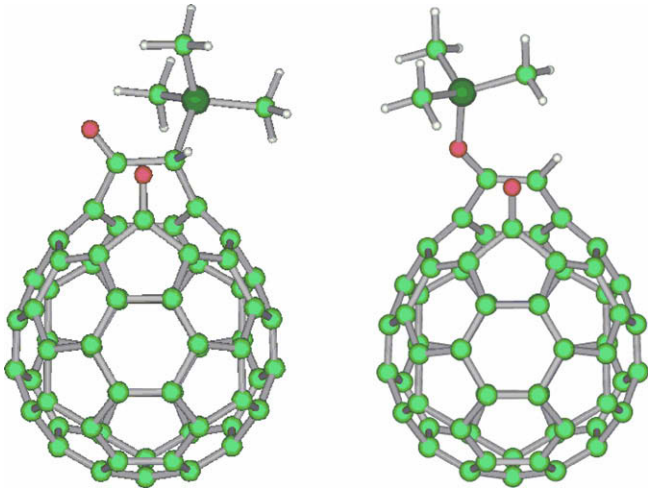


Fig. 7. B3LYP/6-31G optimized structures of **8a** (left) and **9a** (right).

chemical shifts of carbonyl carbons at 213 ppm and enol carbons at 119 and 159 ppm for **9a** are comparable with experimental values of **9b**, while the calculated values for **8a** of carbonyl carbons at 202, 210 ppm and methine carbon at 69 ppm are not.

In conclusion, the unique diastereoselective formation of silyl fulleroid has been accomplished. The origin of the diastereoselectivity is understood in terms of minimization of the repulsive interaction between the silyl groups and the N_2 moiety in the decomposition of the pyrazoline intermediate, based on theoretical calculations. The bridgehead C=C double bond of the silyl fulleroid showed reactivity toward electrophiles such as $^1O_2$, based on POAV analyses. $^1O_2$ oxygenation of silyl fulleroids affords the silyl enol ether derivatives via 1,3-silyl migration of the diketone derivatives.

3. Experimental

3.1. General data

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 and JEOL JNM-ECP500 operating at 500 or 125 MHz, respectively. IR spectra were recorded on a JASCO FT/IR-4100. Mass spectra were recorded on a JEOL SX102A, JEOL JMS-AX505H and Shimadzu AXIMA-CFR. UV spectra were recorded on a JASCO V-550. GPLC (gel permeation liquid chromatography) was performed on an LC-908 (Japan Analytical Industry, Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene). Melting points were determined using a Yanaco MP-S3.

3.2. Materials

Me_3SiCHN_2 (**1a**), $Me_2PhSiCHN_2$ (**1b**), $(3,4\text{-}(OMe)_2C_6H_4Me_2\text{-}SiCHN_2)$ (**1c**) and Ph_3SiCHN_2 (**1d**) were prepared by published procedure [11]. Because of the instability of silyldiazo compounds except **1d**, they were used as ether solution without further purification. $(Me_3Si)_2CN_2$ (**4a**) and $Me_3SiCN_2SiMe_2SiMe_3$ (**4b**) were prepared using **1a** or phenyldiazomethane followed by coupling with Me_3SiCl, Me_3SiCN_2Ph (**4c**), Me_3SiMe_3SiCl [7,12,13] .

3.3. Reaction of monosilyldiazomethane with C_{60}

3.3.1. Trimethylsilyldiazomethane (*1a*) with C_{60}

To a solution of C_{60} (50 mg, 0.069 mmol) in toluene (25 ml) was added a solution of **1a** (17 mg, 0.15 mmol) in ether at room temperature. The mixture was stirred for 30 h. After removal of the solvent under reduced pressure, the crude product was purified by gel permeation liquid chromatography (GPC) to afford 19 mg of **3a** (34%) as a dark brown solid together with the bis- and tris-adducts (15 mg and 15 mg) in 24% and 22% yields (Table 1).

For **3a**: ^{1}H NMR (400 MHz, C_6D_6:CS_2 = 1:1) δ 0.51 (s, 9H), 2.47 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6: CS_2 = 1:1) δ *−0.32* (q), 40.47 (d), 133.02, 136.76, 137.64, 137.85, 138.17, 138.62, 140.06, 140.13, 141.50, 142.11, 142.98, 143.09, 143.18, 143.33, 143.36, 143.50, 143.54, 143.57, 143.66, 143.77, 143.82, 143.95, 144.04, 144.34, 145.25, 145.32, 148.52; ^{29}Si NMR (80 MHz, C_6D_6: CS_2 = 1:1) δ 7.83; UV–vis (cyclohexane) λ_{max}/nm (ε) 539 (250); MS (FAB) calcd for $C_{64}H_{10}Si$ (M^+), 806, found, 806.

3.3.2. Dimethylphenylsilyldiazomethane (*1b*) with C_{60}

To a solution of C_{60} (60 mg, 0.083 mmol) in toluene (25 ml) was added a solution of **1b** (21 mg, 0.12 mmol) in ether at room temperature. The mixture was stirred for 40 h. After removal of the solvent under reduced pressure, the crude product was purified by GPC to afford 30 mg of **3b** (41%) as a dark brown solid together with the bis- and tris-adducts (25 mg and 7 mg) in 29% and 8% yield (Table 1).

For **3b**: ^{1}H NMR (400 MHz, C_6D_6: CS_2 = 1:1) δ 0.75 (s, 6H), 2.69 (s, 1H), 7.25–7.61 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6: CS_2 = 1:1) δ*−1.92* (q), 40.32 (d), 128.25 (s), 128.53 (d), 130.37 (d), 133.62 (d), 135.14, 136.21, 136.81, 137.60, 137.87, 138.10, 138.62, 139.56, 140.15, 141.52, 142.13, 142.97, 143.13, 143.17, 143.29, 143.35, 143.52, 143.56, 143.66, 143.82, 143.97, 144.04, 144.32, 144.36, 145.42, 148.55; ^{29}Si NMR (80 MHz, C_6D_6: CS_2 = 1:1) δ 0.90; UV–vis (cyclohexane) λ_{max}/nm (ε) 536 (1200); MS (FAB) calcd for $C_{69}H_{12}Si$ (M^+), 868, found, 868.

3.3.3. Dimethylveratrylsilyldiazomethane (*1c*) with C_{60}

To a solution of C_{60} (72 mg, 0.10 mmol) in toluene (50 ml) was added a solution of **1c** (1.0 ml, 0.13 mmol) in ether at room temperature. The mixture was stirred for 15 h. After removal of the solvent under reduced pressure, the crude product was purified by GPC to afford 44 mg of **3c** (41%) as dark brown solid together with the bis- and tris-adducts (38 mg and 28 mg) in 29% and 18% yields (Table 1).

For **3c**: ^{1}H NMR (500 MHz, C_6D_6: CS_2 = 1:1) δ 0.62 (s, 6H), 2.69 (m, 1H), 3.59 (s, 3H), 3.64 (s, 3H), 6.72 (d, 1H), 7.07 (s, 1H), 7.16 (d, 1H); ^{13}C NMR (125 MHz, C_6D_6: CS_2 = 1:1) δ *−1.48* (q), 40.65 (d), 55.40 (q), 55.92 (q), 112.30 (d), 116.02 (d), 126.64, 128.30, 132.94, 136.17 (s), 136.66 (s), 137.48, 137.62 (s), 137.94, 138.53, 139.88, 140.05, 141.43, 142.05, 142.94, 143.05, 143.11, 143.13, 143.22, 143.28, 143.46, 143.48, 143.50, 143.61, 143.69, 143.74, 143.78, 143.89, 143.98, 144.26, 144.29, 145.22, 145.25, 148.52, 149.64 (s), 151.93 (s); ^{29}Si NMR (60 MHz, C_6D_6: CS_2 = 1:1) δ *−13.92;* MS (FAB) calcd for $C_{71}H_{16}O_2Si$ ($[M+H]^+$), 929, found, 929.

3.3.4. Triphenylsilyldiazomethane (*1d*) with C_{60}

To a solution of C_{60} (72.0 mg, 0.10 mmol) in toluene (50 ml) was added a solution of **1d** (30.1 mg, 0.10 mmol) in toluene (5 ml). The reaction mixture was refluxed at 110 °C for 24 h. After the removal of the solvent under reduced pressure, the crude product was purified by GPC to afford 14.5 mg in 17.4% yield of ca 1:2 mixture of **7** and **3d** as a dark brown solid together with the bis- and tris-adducts (15.4 and 17.6 mg) in 12.2% and 24.0% yields (Table 1).

For **3d+7**: ^{1}H NMR (500 MHz, C_6D_6: CS_2 = 1:1) δ 3.48, 4.01, 7.26–7.36, 7.74–7.76, 7.95–7.97; ^{13}C NMR (125 MHz, C_6D_6: CS_2 = 1:1) δ 28.4 (d), 38.0 (d), 72.9 (s), 128.6 (s), 130.2, 130.8 (d), 130.9 (s), 132.77, 132.82, 133.0, 134.9, 135.3, 136.1, 136.67 (d), 136.70 (d), 136.9, 137.0, 137.2, 137.7, 138.2, 138.4, 139.4, 140.1, 140.8, 141.3, 141.5, 141.6, 142.2, 142.3, 142.4, 142.9, 143.0, 143.07, 142.12, 143.16, 143.20, 143.3, 143.4, 143.45, 143.48, 143.51, 143.6, 143.7, 143.81,

143.82, 143.9, 144.0, 144.2, 144.3, 144.6, 144.7, 144.8, 145.0, 145.25, 145.33, 145.8, 146.0, 148.6, 150.0, 152.6; ^{29}Si NMR (60 MHz, C_6D_6: CS_2 = 1:1) δ *−13.92;* MS (FAB) calcd for $C_{79}H_{16}Si$ (M^+), 992, found, 992.

A mixture of C_{60} (50 mg, 0.069 mmol) and **1d** (63 mg, 0.21 mmol) in *o*-dichlrobenzene (5 ml) was heated at 90 °C for 6 h. After removal of the solvent under reduced pressure, the crude product was purified by GPC to afford 10 mg of **3d** (19%) as a dark brown solid.

For **3d**: ^{1}H NMR (500 MHz, $CDCl_3$: CS_2 = 2:3) δ 3.43 (s, 1H), 7.27–7.53 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$: CS_2 = 2:3) δ 37.46, 124.91, 127.74, 128.15, 129.51, 129.89, 130.50, 132.30, 132.35, 134.78, 136.21, 136.40, 136.53, 136.65, 137.19, 137.32, 137.76, 137.90, 139.61, 140.96, 141.66, 142.41, 142.57, 142.61, 142.63, 142.68, 142.82, 142.92, 142.98, 143.08, 143.18, 143.34, 143.41, 143.69, 143.79, 144.77, 148.13; MS (MALDI) calcd for $C_{79}H_{16}Si$ (M^+), 992, found, 992.

3.4. Reaction of bissilyl and silylphenyldiazomethane with C_{60}

3.4.1. Bistrimethylsilyldiazomethane (*4e*) with C_{60}

A mixture of C_{60} (20 mg, 0.028 mmol) and **4e** (21 mg, 0.11 mmol) in *o*-dichlrobenzene (10 ml) was degassed and sealed in a pyrex tube. The reaction mixture was heated at 110 °C for 12 h. After removal of the solvent under reduced pressure, the residue was separated by GPC to afford 8 mg of recovered C_{60}.

A solution of C_{60} (10 mg, 0.014 mmol) and **4e** (25 mg, 0.13 mmol) in toluene (10 ml) was degassed and sealed in a pyrex tube. The reaction mixture was irradiated with a high pressure mercury lamp using a glass filter (cut off 350 nm) for 6 h. After removal of the solvent under reduced pressure, the residue was separated by GPC to afford 7 mg of recovered C_{60}.

3.4.2. Pentamethyldisilyltrimethylsilyldiazomethane (*4f*) with C_{60}

A mixture of C_{60} (10 mg, 0.014 mmol) and **4f** (31 mg, 0.13 mmol) in *o*-dichlorobenzene (10 ml) was degassed and sealed in a pyrex tube. The reaction mixture was heated at 155 °C for 30 h. After removal of the solvent under reduced pressure, the residue was separated by GPC to afford 7 mg of recovered C_{60}.

A solution of C_{60} (10 mg, 0.014 mmol) and **4f** (95 mg, 0.39 mmol) in toluene (10 ml) was degassed and sealed in a pyrex tube. The reaction mixture was irradiated for 36 h. After removal of the solvent under reduced pressure, the residue was separated by GPC to afford 47 mg of **5** as colorless crystals in 56% yield.

For **5**: ^{1}H NMR (500 MHz, C_6D_6) δ 0.32 (s, 36H), 0.53 (s, 12H); ^{13}C NMR (125 MHz, C_6D_6) δ 8.02 (q), 9.16 (q), 13.2 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ *−1.78,* 4.23; MS (EI) calcd for $C_{18}H_{48}Si_6$ ($[M-CH_3]^+$), 417, found, 417.

3.4.3. Phenyltrimethylsilyldiazomethane (*4 g*) with C_{60}

To a solution of C_{60} (72.0 mg, 0.10 mmol) in toluene (50 ml), was added a solution of **4g** (35 mg, 0.18 mmol) in toluene (10 ml). The reaction mixture was refluxed at 110 °C for 25 h. After removal of the solvent under reduced pressure, the crude product was purified by GPC to afford 30.4 mg of **6** (46%) as a dark brown solid. The bis- and tris-adducts (10.0 mg and 7.8 mg) were obtained in 13% and 9% yields, respectively, based on the molecular ions peaks (1045 (M^++H) and 1207 (M^+)) from mass spectroscopy.

For **6**: ^{1}H NMR (400 MHz, C_6D_6: CS_2 = 1:1) δ 0.46 (s, 9H), 7.00–7.40 (m, 3H), 7.62–7.64 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6: CS_2 = 1:1) δ 1.52 (q), 48.02 (s), 78.14 (s), 127.16 (d), 128.25 (d), 133.00 (d), 138.28 (d), 138.4, 139.03, 140.91, 141.16, 142.08, 142.32, 142.41, 143.19, 143.24, 143.36, 143.56, 144.10, 144.18, 144.37, 144.72, 144.82, 145.16, 145.39, 145.45, 146.31, 149.95, 150.32; ^{29}Si NMR (60 MHz, C_6D_6: CS_2 = 1:1) δ 9.03; MS (FAB) calcd for $C_{70}H_{15}Si$ ($[M+H]^+$), 883, found, 883.

3.5. Photooxygenation of silylfulleroid *3a,b*

3.5.1. Photooxygenation of silylfulleroid *3a*

A solution of **3a** (58.7 mg, 0.07 mmol) in *o*-dichlorobenzene (20 ml) in a pyrex tube was irradiated with a halogen lamp under bubbling oxygen for 4 h. After removal of the solvent under reduced pressure, an insoluble powder was filtered off. Purification of the residue by GPC gave 9.3 mg of **9b**, as a dark brown solid in 15% yield.

For **9a**: ^{1}H NMR (500 MHz, $CDCl_3$: CS_2 = 1:1) δ 0.57 (s, 9H), 5.87 (s, 1H); IR (KBr) $\tilde{\nu}$ = 1733, 1100 cm^{-1}; MS (MALDI) calcd for $C_{64}H_{10}O_2Si$ ($[M+H]^+$), 839, found, 839.

3.5.2. Photooxygenation of silylfulleroid *3b*

A solution of **3b** (130.0 mg, 0.15 mmol) in *o*-dichlorobenzene (40 ml) in a pyrex tube was irradiated with a halogen lamp under bubbling oxygen for 5 h. After removal of the solvent under reduced pressure, an insoluble powder was filtered off. Purification of the residue by GPC gave 18.7 mg of **9b**, as a dark brown solid in 12% yield.

For **9b**: ^{1}H NMR (500 MHz, $CDCl_3$: CS_2 = 1:1) δ 0.84 (s, 3H), 0.85 (s, 3H), 5.90 (s, 1H), 7.39–7.83 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$: CS_2 = 1:1) δ 0.88, 97.68, 127.48, 130.06, 130.36, 133.82, 135.13, 135.29, 135.43, 135.75, 135.93, 136.12, 137.00, 137.26, 137.49, 137.67, 138.57, 138.97, 139.23, 139.63, 140.16, 141.63, 141.76, 142.06, 142.28, 142.70, 142.92, 143.01, 143.10, 143.14, 143.30, 143.39, 143.72, 143.93, 144.41, 144.86, 145.27, 145.63, 145.70, 145.74, 145.77, 145.86, 146.08, 146.32, 146.62, 147.08, 147.05, 145.08, 147.21, 147.39, 147.85, 148.14, 148.47, 148.59, 149.98, 150.33, 199.76; IR (KBr) $\tilde{\nu}$ = 1733, 1100 cm^{-1}; MS (MALDI) calcd for $C_{69}H_{12}O_2Si$ ($[M+H]^+$), 901, found, 901.

3.6. Computational studies

Calculations were carried out on an HPC-P4/GLW and HPC3000-XC104T workstation provided by HPC Inc. of Japan. Ab initio calculations were performed using the Gaussian 03 computer program [14]. The initial geometries for the pyrazolines, fulleroids and oxygenation products were constructed using the Chem 3D graphical interface provided by Cambridge Software Inc. All geometry optimizations were performed on cartesian coordinate using the energy gradient minimization method. Transition states were formed by the QST2 technique in the Gaussian 03 program. The vibrational analyses were carried out using the MolStudio R4 graphical interface from NEC. The POAV/3D-HMO analyses were performed using the POAV3 program [8c].

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