Methano- and Propanofullerenes by [1+2] and [3+2] Cycloadditions of Vinylcarbene Species

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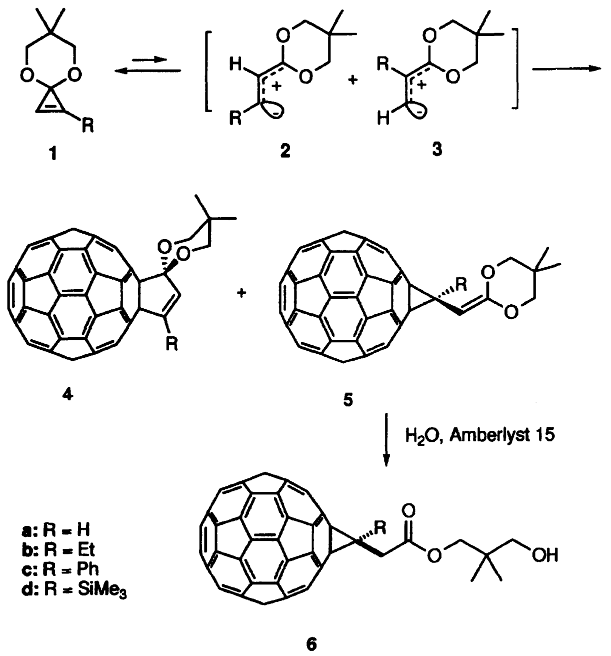
Vinylcarbene species generated by thermolysis of cyclopropenone acetal (CPA) reacts with C_{60} in a [1+2] and a [3+2] manner to afford, at 80 °C, methano- and propanofullerene derivatives as a 10 : 1 mixture. The periselectivity depends on the reaction temperature; the ratio of the [1+2] and [3+2] cycloadducts changed to 2 : 1 and to 7 : 93 in the reaction at 100 and 140 °C, respectively. Temperature dependence was also observed in the reaction of phenyl-substituted CPA. The reactions of ethyl- and trimethylsilyl-substituted CPAs, which proceeded only at 150—170 °C, afforded propanofullerenes as a sole product. The reaction of the substituted CPAs proceeded exclusively via a terminally substituted vinylcarbene species.

Organic functionalization of buckminsterfullerenes[1] is vital for the fullerene science and technology, as exemplified by the conspicuous biochemical activity of water-soluble fullerene carboxylic acids[2] and fullerene–DNA conjugates.[3] Among various candidates of organic reactions to be used for fullerene functionalization, thermal cycloadditions have proved to be particularly useful.[4] Thus, [1+2],[5—7] [2+2],[8] and [4+2][9] cycloaddition reactions have been successfully employed for the synthesis of three, four, and six-membered rings fused to C_{60}. In contrast, [3+2] routes to propanofullerenes (i.e., cyclopentane fused to C_{60}) are still rare[10] because of the general lack of suitable three-carbon cycloaddition reagents.[11] We report, in this article, that an efficient synthesis of propanofullerene can be achieved by the reaction of vinylcarbene species (**2** and **3**) generated by thermolysis of cyclopropenone acetals (CPAs, **1**) (Eq. 1).[12—14]



(1)

Table 1. Temperature-Dependence of the [3+2] and [1+2] Cycloadditions

$$\mathbf{1a} \xrightarrow[\substack{o-\mathrm{Cl_2C_6H_4} \\ 80^\circ\mathrm{C},\ 3\ \mathrm{d}}]{\mathrm{C_{60}}\ (1\ \mathrm{equiv})} \mathbf{4a}+\mathbf{5a}$$

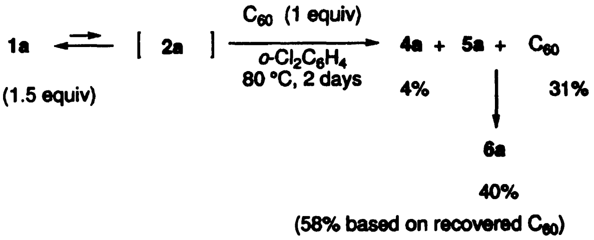
Temp (°C)	Equiv	[3+2] : [1+2][a]	Yield of main product (%)
80	1.9	9 : 91	44
80[b]	1.4	8 : 92	—[c]
100	1.4	33 : 67	22
140	1.4	93 : 7	31

a) The ratio was determined by HPLC. b) Toluene was used as a solvent. c) Not determined.

Results and Discussion

Cycloaddition and Temperature Effects. Upon heating around 80 °C, the parent CPA **1a** undergoes cleavage of the C–C σ bond to generate reversibly the vinylcarbene species **2a**. The nature of this carbene species has been examined by its cycloaddition behavior[12] and by kinetic and thermodynamic trapping with water.[13] The carbene species has been shown to be a polarized singlet species and undergoes cycloaddition to electron-deficient olefins either in a [1+2] or a [3+2] manner. The periselectivity was strictly dependent on the nature of the acceptor; the [1+2] reaction with acrylic esters and the [3+2] reaction with more electron-deficient olefins such as alkylidenemalonates.

Thus it was surprising that, when a mixture of the CPA **1a** (1.5 equiv) and C_{60} (100 mg) in *o*-dichlorobenzene (90 ml) was heated at 80 °C for 2 d, we obtained a small amount (4% yield) of the [3+2] cycloadduct **4a** together with a reddish major product **6a** in 40% yield (58% based on recovered C_{60}) after treatment of the hydrolytically labile ketene acetal **5a** in the presence of Amberlyst 15 (Eq. 2). The use of more than two equivalents of CPA did not improve the yield of **6a**, but instead produced a considerable amount of multiadducts. The polar ester **6a** can be readily separated from the less polar C_{60} and **4a** by routine silica gel column chromatography.



(2)

Upon further examination of the reaction conditions, we found that the [3+2]/[1+2] ratio increases dramatically by raising the reaction temperature. The reaction was undertaken at 80, 100, and 140 °C and the ratio of [3+2] and [1+2] adducts was determined by HPLC and ^{1}H NMR analysis of the crude products. The reaction at 80 °C afforded a 1:10 mixture of [3+2] and [1+2] cycloadducts, and the ratio changed to 1:2 then to 93:7 in the reactions at 100 and 140 °C, respectively (Table 1). Changing the solvent to toluene did not affect the ratio.

While it is possible that the formation of the [3+2] cycloadduct **4** is due to vinylcyclopropane rearrangement of the [1+2] cycloadduct **5**, a control experiment excluded this possibility.[15] Thus, a mixture of an unsubstituted cyclopropenone acetal **1a** and C_{60} was heated at 80 °C for 2 d to obtain a mixture of **4a** and **5a**, which was subsequently heated at 140 °C for an additional 2 d. The 9:91 ratio of **4a** and **5a** did not change throughout the reaction.

The present vinylcarbene chemistry rests on the availability of substituted carbene species.[16] We thus examined the reaction of ethyl- (**1b**), phenyl- (**1c**), and silyl- (**1d**) substituted CPAs with C_{60}.

$$\mathbf{1b,d} \rightleftarrows [\,\mathbf{2}\,] \xrightarrow[o\text{-}Cl_2C_6H_4]{C_{60}} \mathbf{4}$$

R	Eq.	Temp (°C)	Time (h)	Yield (%)
Et	1.2	150	48	40 (69)[a]
$SiMe_3$	1.9	170	72	52 (78)[a]

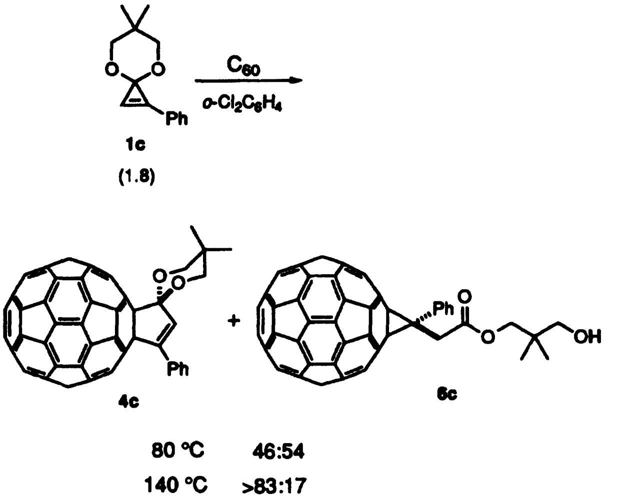
a) Based on recovered C_{60}

(3)

Carbene formation is slow for the ethyl CPA **1b**.[13] Thus, **1b** was heated at 150 °C with C_{60} to give the [3+2] cycloadduct **4b** in 40% yield as a sole product. While it has been shown that, under these conditions, both the internally (**3b**) and the terminally (**2b**) substituted carbene species form reversibly from **1b**,[13] only one regioisomer (**4b**) formed, indicating that the terminally substituted carbene **2b** is more reactive than **3b**.

The reaction of the trimethylsilyl CPA **1d** proceeded at 170 °C and gave exclusively the [3+2] adduct **4d** via terminally substituted vinylcarbene. The high temperature required in this case must be due to high activation energy of the cycloaddition stage rather than the carbene formation stage, since the latter has been shown to take place even at 100 °C.[13]

While the ethyl- and silyl-substituted cyclopropenes reacted only at high temperatures, the reaction of the phenyl CPA **1c** took place at 80 °C and thus gave us an opportunity to investigate the temperature effects. Thus, a 1:1 mixture of [3+2] and [1+2] cycloadducts formed at 80 °C, and the former became predominant at 140 °C (Eq. 4). Regardless of substituents, the [3+2] cycloadducts could hence be made as a predominant product by carrying out the reaction at 140—170 °C.



(4)

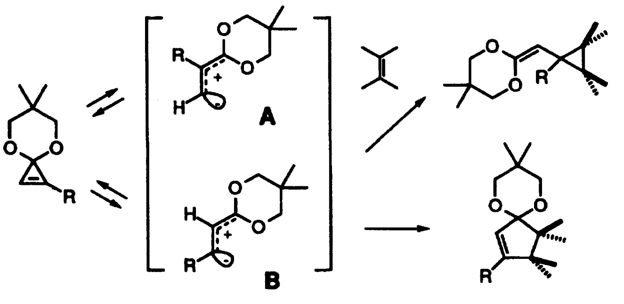
Regiochemistry and Periselectivity of Vinylcarbene Cycloaddition. There are two problems in the cycloaddition of the vinylcarbene species generated from a substituted CPA: the regiochemistry of the cyclopropene ring cleavage and the periselectivity of the cycloaddition (i.e., [3+2] vs. [1+2], Scheme 1).

The regioselectivity observed in the thermal reactions of substituted CPAs with water, olefins and C_{60} has previously been investigated; the results are summarized in Table 2.[13] The selectivity obtained with in situ water quenching reflects the kinetic regioselectivity of the ring opening, namely the selectivity between **A** and **B**, which are in rapid equilibrium with each other. In the cycloadditions with olefins, which is much less reactive

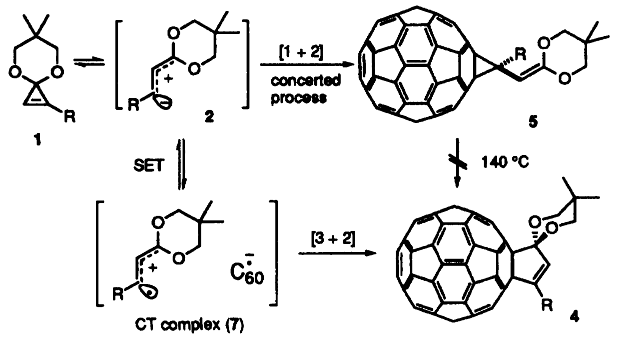
Table 2. Summary of the Regiochemistry of the VC Formation and Cycloadditions of CPA **1** (Approximate Reaction Temperature, °C)[a]

Reactant	R=Ethyl (**1b**)	Phenyl (**1c**)	Me_3Si (**1d**)
Water	b)	58 : 42—33 : 67 (70)	17 : 83 (70)
[1+2] with olefin[c]	9 : 91—2 : 98 (130)	7 : >93—0 : 100 (80)	0 : 100 (170)
[3+2] with olefin[c]	71 : 29 (150)	0 : 100 (75)	0 : 100 (100)
[3+2] with C_{60}[d]	0 : 100 (150)	0 : 100 (80)	0 : 100 (170)

a) The ratios refer to the product ratios correlated to those of internally substituted (**A**) vs. terminally substituted VC isomers (**B**). b) Not determined. c) Taken from Ref. 11. d) This work.



Scheme 1.



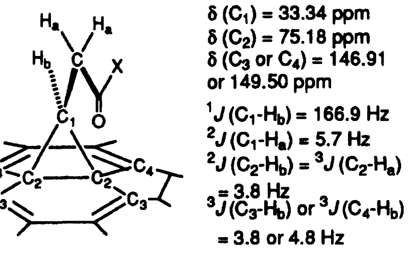
Scheme 2.

than water, the carbene isomers **A** and **B** have time to interconvert via the starting CPA (especially at a low reactant concentration such as the one employed for the C_{60} reaction, 0.2 mM, 1 M=1 mol dm^{-3}). Hence, the regioselectivity of the cycloaddition reflects the kinetic reactivity of the carbene isomers rather than the kinetic ratio of their formation. The regioselectivity observed in the present studies (fourth row in Table 2) fully conforms to this generalization. The terminally substituted isomer **B** is more reactive toward C_{60} regardless of the R substituent. It is yet to be clarified, however, why the terminally substituted isomer is more reactive than the internal one.

The temperature dependence of the periselectivity is also notable. It has been shown by Boger[12)] for the parent CPA that the [3+2] cycloaddition, which takes place with highly electron-deficient olefins, is due to a single electron transfer (SET) mechanism, while the [1+2] cycloaddition may be a straightforward concerted cycloaddition. In view of the high electron affinity of C_{60},[17)] it is reasonable that the [3+2] cycloaddition to C_{60} proceeds via a SET process. It may be noted that neither the mixed periselectivity for a single olefinic substrate nor the temperature dependent change of periselectivity has been observed for usual olefinic substrates. A proposed mechanism of the cycloaddition reaction with C_{60} is depicted in Scheme 2. The dividing point between the concerted [1+2] and the SET [3+2] paths may depend on the steric effects of C_{60} and the R substituent. The latter process more likely tolerates steric encumberment than the former whose transition state must be more rigid (thus with larger negative entropy of activation).

Structure Determination. Since the structure of carbene transfer reactions aroused considerable debate at the time when the present studies were initiated,[5,6)] we paid special attention in the structural examination of **6**, and assigned the [6.6]-methanofullerene structure[7)] in the light of spectral (vide infra) and theoretical analysis.[14,18)] Concomitant with the present studies, the 6,6-methanofullerene structures have been assigned to the products of related carbene transfer reactions.[5,6)] The (alkoxycarbonyl)methyl structural moiety in **6a** was readily identified by the ^{1}H NMR spectrum. The signal (H_a, δ=3.64) due to the two equivalent protons at the α position of the alkoxycarbonyl group is coupled (doublet, J=7.3 Hz) to the adjacent cyclopropyl methine proton (H_b, δ=4.44, triplet, J=7.3 Hz). The unusual downfield-shift of the cyclopropyl methine proton is due to the magnetic deshielding effect induced by local ring currents in C_{60}.[19)]

The ^{13}C NMR spectra were vital for the assignment of the methanofullerene structure (Fig. 1). The pro-



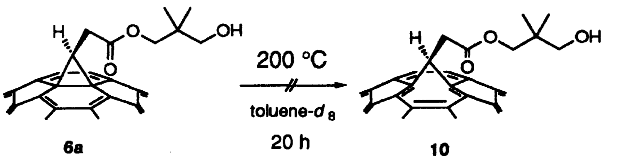
6a

Fig. 1. ^{13}C NMR data for the cyclopropane structure in **6a**.

ton-decoupled ^{13}C NMR spectra showed only 39 signals, indicating C_s symmetry of the molecule. Of the 32 carbon signals assigned to the C_{60} skeleton, 27 signals of relative intensity of 2 and 4 signals of intensity of 1 are due to sp^2 carbons; a 2-carbon intensity signal at $\delta=75.18$ is due to the sp^3 C_2 carbon and suggestive of the cyclopropane structure. The C–H coupling in the proton-non-decoupled ^{13}C NMR spectra was the most crucial for the identification of the cyclopropane structure in **4a**. The C_1 atom ($\delta=33.34$), which is directly connected to H_b, was found to exhibit a very large $^1J_{\mathrm{C-H}}$ coupling of 166.9 Hz. This J value is incompatible with the fulleroid structure, as compared with values recorded for 4a,8a-methanonaphthalene **8** and the 1,6-methano[10]annulene **9** (Chart 1).[20] The signal at $\delta=75.18$ with relative intensity of two carbons appears as quartet ($J=3.8$ Hz) with two- and three-bond coupling to H_b and H_a, and can thus be assigned to the C_2 atom at the cyclopropane/C_{60} juncture. We could also assign two signals appearing in the "aromatic region" at $\delta=146.91$ ($J=3.8$ Hz) and 149.05 ($J=4.8$ Hz) to C_3 and C_4,[21] since they exhibit three-bond coupling with H_b. The ^{13}C NMR spectra does not conclusively identify the location of the cyclopropane ring, but the [6.6]-ring junction was tentatively assigned by the known reactivity pattern of the C_{60}, as well as by the fact that only a single diastereomer of **6a** formed by the reaction.

The UV-visible spectrum of **6a** (Fig. 2) ($\lambda=259$, 326, 428, 490, and 688 nm) was found to be virtually identical with those previously assigned to the sugar-connected methanofullerene[5] ($\lambda=433$ and 499 nm) and fullerene epoxide[22] ($\lambda=256$, 328, 424, 496, and 680 nm).

The methanofullerene **6a** is thermally stable and does not isomerize to **10** upon heating in toluene-d_8 at 200 °C for 20 h, as monitored by ^{1}H NMR (Eq. 5).[23]



(5)

Structure of the [3+2] adduct **4** was assigned by NMR spectra. For instance, the ^{13}C NMR spectrum (1 : 1 CS_2/$CDCl_3$) of the cycloadduct **4b** showing only 38 signals (31 at $\delta=110$—155 region), as well as the ^{1}H NMR spectrum showing a symmetrical acetal structure, indicated the C_s symmetry of the molecule and therefore the ring fusion at the [6.6]-ring juncture. Irradiation of the axial acetal protons caused 18% nuclear Overhauser enhancement of the olefinic proton signal, clearly indicating the 3-ethylcyclopent-2-en-1-one structure, as shown below (Fig. 3).

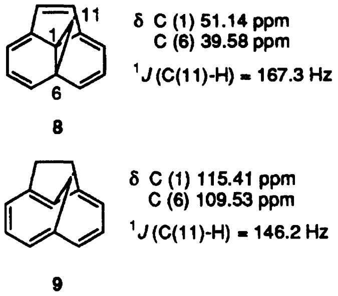


Chart 1.

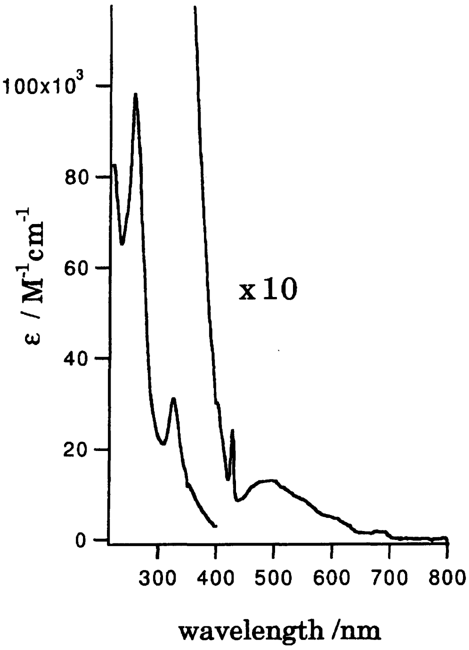


Fig. 2. UV-visible spectra of **6a** in cyclohexane.

Conclusion

The thermal cycloaddition reactions of vinylcarbenes have been found to produce novel fullerene derivatives, methano- and propanofullerenes. These derivatives are not only intriguing from the structural point of view, but also synthetically useful for further derivatization using the functional groups introduced.[24] The starting CPAs being readily available, the present reactions provide access to a variety of fullerene derivatives. It is worthwhile noting that CPAs are stable non-explosive carbene precursors that can be used widely for functionalization of fullerenes.

Experimental

General. All reactions dealing with air- and moisture-sensitive compounds were undertaken in a dry reaction vessel under nitrogen stream. Infrared spectra were

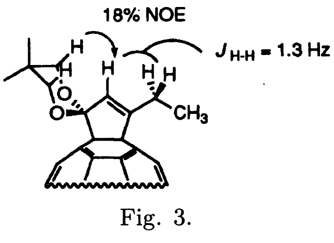


Fig. 3.

recorded on a JASCO IR-800; absorptions are reported in cm^{-1}. ^{1}H NMR spectra was taken at 200, 270, 400, or 500 MHz and ^{13}C NMR spectra were taken at 50, 67.5, 100, 125 MHz using JEOL FX-200, GSX-270, EX-400, or GSX-500 instrument, and are reported in parts per million from internal tetramethylsilane for ^{1}H NMR and CDCl$_3$ for ^{13}C NMR. Routine flush chromatography on silica gel was performed on Kieselgel 60 (Merck). Analytical thin layer chromatography was carried out using Merk precoated, glassbacked Kiesel 60 F$_{254}$ plates. Gel permeation chromatography was performed on a Japan Analytical Industry LC-908 machine equipped with JAIGEL-1H (20×600 mm) and -2H (20×600 mm) GPC columns.[25] High pressure liquid chromatography was performed on a Shimadzu LC10A machine equipped with YMC-Pack ODS-A (250×10 mm i. d.).

Material. Toluene and *o*-dichlorobenzene were distilled from calcium hydride under nitrogen and stored over molecular sieves. The synthesis of fullerene arc soot was carried out as reported in the literature.[26] Purification of the crude fullerene extracted from carbon arc soot containing 70—85% C$_{60}$ and 10—15% C$_{70}$ was carried out on a column of decolorizing carbon Norit-A/silica gel.[27] Purity of the C$_{60}$ was checked by HPLC analysis (ODS, 30% *i*-PrOH/hexane, flow rate 1 ml min^{-1}, retention time 35 min).

[1+2] Cycloaddition of CPA (1a) to C$_{60}$. Methanofullerene 6a. To a solution of C$_{60}$ (100 mg, 138 µmol) in *o*-dichlorobenzene (90 ml) was added **1a** (29 µl, 208 µmol). The mixture was stirred at 80 °C for 24 h. The solvent was removed by distillation (ca. 2 mmHg, 50 °C) and the black residue was redissolved in a mixture of toluene and CHCl$_3$. Amberlyst 15 (ca. 100 mg) and 100 µl of water were added to the mixture and the suspension was stirred at room temperature for 0.5 h. Amberlyst 15 was removed by filtration and the filtrate was concentrated to give a crude product. Purification was achieved by silica gel column chromatography. The initial elution with hexane afforded unreacted C$_{60}$ (31.4 mg, 31% recovery). The [3+2] adduct was obtained by elution with 30% toluene in hexane. The [1+2] cycloadduct **6a** was obtained by elution with 10% EtOAc in toluene (50.1 mg, 44% yield, 58% based on recovered C$_{60}$; R_f=0.20, 10% EtOAc in toluene). The ratio of the [1+2] and the [3+2] adduct was determined by analytical HPLC (ODS, 30% *i*-PrOH/hexane, flow rate 1 ml min^{-1}, retention times of [1+2] and [3+2] cycloadduct are 15.1 and 20.8 min, respectively). Further purification was carried out on a recycling preparative GPC (CHCl$_3$): UV-vis [cyclohexane, $\lambda_{\max}$ (log ε)] 326 (4.57), 402 (3.49), 428 (3.40), 490 (3.13), 688 (2.59); IR (CHCl$_3$) 3625, 2925, 2870, 1730, 1430, 1380, 1190, 1040, 580, 530; ^{1}H NMR (CDCl$_3$) δ=1.03 (s, 6 H, two CH_3), 1.98 (br s, 1 H, OH), 3.45 (s, 2 H, CH_2OH), 3.64 (d, J=7.3 Hz, 2 H, CH_2CO$_2$), 4.21 (s, 2 H, CO$_2$CH_2), 4.44 (t, J=7.3 Hz, 1 H, CHCH$_2$); ^{13}C NMR (CDCl$_3$) δ=21.61 (two CH$_3$), 31.84 (CH$_2$), 33.34 (CH), 36.54 (C), 68.37 (CH$_2$), 70.33 (CH$_2$), 75.18 (C$_{60}$, 2 C, cyclopropyl carbon), 136.34 (C$_{60}$, 2 C), 137.97 (C$_{60}$, 2 C), 141.11 (C$_{60}$, 2 C), 141.12 (C$_{60}$, 2 C), 142.15 (C$_{60}$, 2 C), 142.17 (C$_{60}$, 2 C), 142.37 (C$_{60}$, 2 C), 142.65 (C$_{60}$, 2 C), 413.02 (C$_{60}$, 3 C), 143.05 (C$_{60}$, 2 C), 143.10 (C$_{60}$, 3 C), 143.65 (C$_{60}$, 2 C), 143.73 (C$_{60}$, 2 C), 144.30 (C$_{60}$, 2 C), 144.40 (C$_{60}$, 2 C), 144.42 (C$_{60}$, 2 C), 144.57 (C$_{60}$, 1 C), 144.71 (C$_{60}$, 2 C), 144.79 (C$_{60}$, 1 C), 144.81 (C$_{60}$, 2 C), 145.10 (C$_{60}$, 2 C), 145.19 (C$_{60}$, 4 C), 145.20 (C$_{60}$, 2 C), 145.25 (C$_{60}$, 2 C), 145.72 (C$_{60}$, 2 C), 146.91 (C$_{60}$, 2 C), 149.50 (C$_{60}$, 2 C), 171.26 (C=O). Found: C, 85.29; H, 1.31%. Calcd for C$_{68}$H$_{14}$O$_3$· 3/4 CHCl$_3$: C, 85.27; H, 1.54%.

Propanofullerene 4a. R_f=0.55 (50% toluene in hexane); IR (CS$_2$) 2950, 2850, 1180, 1140, 1110, 1020, 830, 760, 530; ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1) δ=1.00 (s, 3 H, CH$_3$), 1.39 (s, 3 H, CH$_3$), 3.98 (d, J=11.5 Hz, 2 H, CH$_2$O), 4.20 (d, 2 H, J=11.5 Hz, CH$_2$O), 7.32 (d, J=6.2 Hz, CH=CH), 7.55 (d, J=6.2 Hz, CH=CH); ^{13}C NMR (CDCl$_3$/CS$_2$ 2/1) δ=21.90, 22.83, 29.87, 73.51, 74.22, 77.86, 114.98, 126.93, 134.86, 136.69, 139.25, 139.56, 140.09, 141.43, 141.59, 141.70, 141.90, 142.09, 142.23, 142.29, 142.43, 142.87, 144.17, 144.50, 144.90, 145.00, 145.18, 145.34, 145.75, 145.82, 145.89, 146.17, 146.75, 147.19, 153.55, 154, 78. Found: C, 92.55; H, 1.35%. Calcd for C$_{68}$H$_{14}$O$_3$· 1/5CHCl$_3$: C, 92.59; H, 1.39%.

[3+2] Cycloaddition of Ethyl CPA (1b) to C$_{60}$. Propanofullerene 4b. To a solution of C$_{60}$ (100 mg, 0.14 mmol) in *o*-dichlorobenzene (90 ml) was added **1b** (30 µl, 0.17 mmol). The mixture was stirred at 150 °C for 2 d. The solvent was removed by distillation (50 °C, ca. 2 mmHg). Silica gel column chromatograph was performed to isolate the product. Unreacted C$_{60}$ was recovered (42 mg, 42%) by elution with hexane, and elution with 30% toluene in hexane gave **4a** (50 mg, 40%; 69% based on recovery): R_f=0.41 (50% hexane in toluene); IR (CS$_2$) 2950, 2925, 2850, 1180, 1100, 1020, 760, 520; ^{1}H NMR (CS$_2$/CDCl$_3$ 1/1) δ=0.99 (s, 3 H, CH$_3$), 1.35 (s, 3 H, CH$_3$), 1.57 (t, J=7.2 Hz, 3 H, CH$_2$CH$_3$), 3.08 (dq, J=1.4, 7.2 Hz, 2 H, CH$_2$CH$_3$), 3.84 (d, J=11.5 Hz, 2 H, acetal methylene), 4.18 (d, J=11.5 Hz, 2 H, acetal methylene), 7.13 (t, J=1.3 Hz, 1 H, vinyl H); ^{13}C NMR (CS$_2$/CDCl$_3$ 1/1) δ=12.70, 21.94, 22.87, 22.96, 29.92, 73.42, 79.17, 114.30, 119.34, 134.64, 136.64, 139.64, 139.66, 141.44, 141.54, 141.77, 141.79, 142.11, 142.32, 142.34, 142.49, 142.90, 144.15, 144.53, 144.90, 145.16, 145.28, 145.41, 145.72, 145.82, 145.86, 146.18, 146.48, 146.83, 147.20, 153.87, 154.15, 154.94. Found: C, 89.35; H, 1.55%. Calcd for C$_{70}$H$_{16}$O$_2$·1/2CHCl$_3$: C, 89.26; H, 1.75%.

[3+2] Cycloaddition of Trimethylsilyl CPA (1d) to C$_{60}$. Propanofullerene 4d. To a solution of C$_{60}$ (250 mg, 0.346 mmol) in *o*-dichlorobenzene was added **1d** (150 µl, 0.658 mmol). The purple reaction mixture was stirred at 170 °C for 3 d. The solvent was removed under reduced pressure to give a brown solid (398 mg). Purification was carried out by silica gel column chromatography (silica gel 210 g). Initial elution with hexane gave unreacted C$_{60}$ (82.1 mg, 33%) and subsequent elution with 30% toluene in hexane gave **4d** (167.8 mg, 52%): R_f=0.54 (30% toluene in hexane); IR (CS$_2$) 2950, 2925, 2850, 1400, 1125, 840, 530; ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1) δ=0.04 (s, 9 H, Si(CH_3)$_3$), 0.97 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 3.83 (d, J=11.2 Hz, CHHO), 4.18 (d, J=11.2 Hz, CHHO), 7.61 (s, olefinic CH); ^{13}C NMR (CDCl$_3$/CS$_2$ 1/1) δ=0.71 (si(CH$_3$)$_3$), 21.96 (CH$_3$), 22.86 (CH$_3$), 30.05 (C), 73.56 (OCH$_2$, 2 C), 78.76 (C$_{60}$, C), 79.14 (C$_{60}$, C), 115.41 (C=CHC), 134.68, 136.30, 136.47, 139.42, 138.68, 141.49, 141.59, 141.89, 141.99, 142.14, 142.32, 142.43, 142.52, 142.93, 144.22, 144.57, 144.92, 144.97, 145.24, 145.48, 145.79, 145.89, 145.92, 146.24, 146.26, 146.81, 147.17, 147.25, 154.39, 154.83, 155.64.

The regiochemistry of trimethylsilyl group was determined based on the strong NOE between the acetal methylene group and vinylic proton.

[1+2] Cycloaddition of Phenyl CPA (1c) to C_{60}. Methanofullerene 6c. The reaction was carried out in a similar manner to that described for **4a**. $R_f=0.26$ (10% EtOAc in toluene); IR (CCl_4) 3650, 3550, 2950, 2930, 2870, 1740, 1430, 1380, 1340, 1170, 700, 530; ^{1}H NMR ($CDCl_3$) $\delta=0.90$ (s, 6 H, two CH_3), 1.90 (br s, 1 H, OH), 3.25 (s, 2 H, CH_2OH), 3.99, 4.04 (s, 4 H, CH_2CO_2, CO_2CH_2C), 7.47 (t, $J=7.3$ Hz, 1 H, phenyl CH), 7.54 (t, $J=7.3$ Hz, 2 H, phenyl CH), 8.03 (d, $J=7.3$ Hz, phenyl CH); ^{13}C NMR ($CDCl_3$, phenyl carbons were tentatively assigned) $\delta=21.52$ (2 C, two CH_3), 36.34 (C), 39.82 (CH_2), 47.11 (C), 68.14 (CH_2), 70.14 (CH_2), 79.19 (C_{60}, 2 C, cyclopropyl carbon), 128.56 (C_{60}, 2 C, phenyl), 128.66 (1 C, phenyl), 132.06 (2 C, phenyl), 136.21 (1 C, phenyl), 137.63 (C_{60}, 2 C), 137.88 (C_{60}, 2 C), 140.86 (C_{60}, 2 C), 141.13 (C_{60}, 2 C), 142.14 (C_{60}, 2 C), 142.16 (C_{60}, 2 C), 142.18 (C_{60}, 2 C), 142.34 (C_{60}, 2 C), 142.93 (C_{60}, 2 C), 142.97 (C_{60}, 2 C), 143.00 (C_{60}, 1 C), 143.05 (C_{60}, 2 C), 143.14 (C_{60}, 3 C), 143.78 (C_{60}, 2 C), 143.82 (C_{60}, 2 C), 144.17 (C_{60}, 2 C), 144.56 (C_{60}, 2 C), 144.65 (C_{60}, 3 C), 144.70 (C_{60}, 1 C), 144.72 (C_{60}, 2 C), 144.84 (C_{60}, 2 C), 145.12 (C_{60}, 2 C), 145.25 (C_{60}, 2 C), 145.27 (C_{60}, 4 C), 145.68 (C_{60}, 2 C), 147.86 (C_{60}, 2 C), 148.37 (C_{60}, 2 C), 170.70 (C=O). Found: C, 83.67; H, 1.89%. Calcd for $C_{74}H_{18}O_3\cdot CHCl_3$: C, 83.85; H, 1.78%.

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References

1) Review: R. Taylor, and R. M. Walton, *Nature*, **363**, 685 (1993); A. Hirsch, *Angew. Chem., Int. Ed. Engl.*, **32**, 1138 (1993).

2) H. Tokuyama, S. Yamago, E. Nakamura, T. Shiraki, and Y. Sugiura, *J. Am. Chem. Soc.*, **115**, 7918 (1993).

3) A. Boutorine, H. Tokuyama, M. Takasugi, H. Isobe, E. Nakamura, and C. Hélène, *Angew. Chem., Int. Ed. Engl.*, **33**, 2462 (1994).

4) F. Wudl, *Acc. Chem. Res.*, **25**, 157 (1992); T. Suzuki, Q. Li, K. C. Khenami, F. Wudl, and Ö. Almarsson, *Science*, **254**, 1186 (1991); T. Suzuki, Q. Li, K. C. Khemani, and F. Wudl, *J. Am. Chem. Soc.*, **114**, 7301 (1992); M. Prato, Q. Li, F. Wudl, and V. Lucchini, *J. Am. Chem. Soc.*, **115**, 1148 (1993).

5) A. Vasella, P. Uhlmann, C. A. A. Waldraff, F. Diederich, and C. Thilgen, *Angew. Chem., Int. Ed. Engl.*, **31**, 1338 (1992); M. Tsuda, T. Ishida, T. Nogami, S. Kurono, and M. Ohashi, *Tetrahedron Lett.*, **34**, 6911 (1993); K. Komatsu, A. Kagayama, Y. Murata, N. Sugita, K. Kobayashi, S. Nagase, and T. S. M. Wan, *Chem. Lett.*, **1993**, 2163; T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **115**, 1605 (1993).

6) M. Prato, V. Lucchini, M. Maggini, E. Stimpfl, G. Scorrano, M. Eiermann, T. Suzuki, and F. Wudl, *J. Am. Chem. Soc.*, **115**, 8479 (1993); A. B. Smith, III, R. M. Strongin, L. Brard, G. T. Frust, W. J. Romanow, K. G. Owens, and R. C. King, *J. Am. Chem. Soc.*, **115**, 5829 (1993). L. Issacs, A. Wehrsig, and F. Diederich, *Helv. Chim. Acta*, **76**, 1231 (1993).

7) X-Ray determination of methanofullerene structure: J. Osterodt, M. Nieger, and F. Vogtle, *J. Chem. Soc., Chem. Commun.*, **1994**, 1607.

8) S. H. Hoke, II, J. Molstad, D. Ditettato, M. Jennifer, D. Carlon, B. Kahr, and R. G. Cooks, *J. Org. Chem.*, **57**, 5069 (1992); S. R. Wilson, N. Kaprinidis, Y. Wu, and D. I. Schuster, *J. Am. Chem. Soc.*, **115**, 8495 (1993); X. Zhang, A. Romero, and C. S. Foote, *J. Am. Chem. Soc.*, **115**, 11024 (1993); S. Yamago, A. Takeichi, and E. Nakamura, *J. Am. Chem. Soc.*, **116**, 1123 (1994).

9) V. M. Rotello, J. B. Howard, T. Yadav, M. M. Conn, E. Viani, L. M. Giovane, and A. L. Lafleur, *Tetrahedron Lett.*, **34**, 1561 (1993); Y. Rubin, S. Khan, D. I. Freedberg, and C. Yeretzian, *J. Am. Chem. Soc.*, **115**, 344 (1993); S. I. Khan, S. A. M. Oliver, M. N. P. Row, and Y. Rubin, *J. Am. Chem. Soc.*, **115**, 4919 (1993).

10) M. Prato, T. Suzuki, H. Foroudian, Q. Li, K. Khemani, F. Wudl, J. Leonetti, R. D. Little, T. White, B. Rickborn, S. Yamago, and E. Nakamura, *J. Am. Chem. Soc.*, **115**, 1594 (1993).

11) Reveiw: A. Padwa, "1,3-Dipolar Cycloaddition Chemistry," John Wiley & Sons, New York (1984), Vols. 1 and 2.

12) Review: D. L. Boger and C. E. Brotherton, "Advances in Cycloaddition," ed by D. P. Curran, JAI Press, Greenwich (1990), Vol. 2, p. 147; D. L. Boger and C. E. Brotherton, *J. Am. Chem. Soc.*, **108**, 6695 (1986); D. L. Boger and R. J. Wysocki, Jr., *J. Org. Chem.*, **53**, 3408 (1988).

13) H. Tokuyama, M. Isaka, and E. Nakamura, *J. Am. Chem. Soc.*, **114**, 5523 (1992); H. Tokuyama, T. Yamada, and E. Nakamura, *Synlett*, **1993**, 589.

14) Preliminary communication: H. Tokuyama, M. Nakamura, and E. Nakamura, *Tetrahedron Lett.*, **34**, 7429 (1993).

15) Similar finding was also made for the adduct from simple olefins (see, Ref. 11).

16) M. Isaka, S. Matsuzawa, S. Yamago, S. Ejiri, Y. Miyachi, and E. Nakamura, *J. Org. Chem.*, **54**, 4727 (1989); M. Isaka, R. Ando, Y. Morinaka, and E. Nakamura, *Tetrahedron Lett.*, **32**, 1339 (1991); M. Isaka, S. Ejiri, and E. Nakamura, *Tetrahedron*, **48**, 2045 (1992).

17) P. -M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. J. Whetten, *J. Am. Chem. Soc.*, **113**, 1050 (1991).

18) F. Diederich, L. Issacs, and D. Philip, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 391.

19) Comparison of the proton chemical shift values of the fullerene derivative below (Ref. 9) and cyclopentane analog revealed the significant downfield shift of the protons near C_{60} surface. (^{1}H NMR chemical shift in ppm). (Fig. 4).

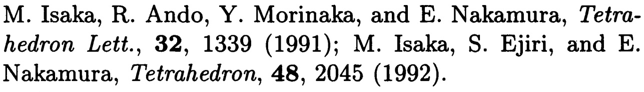

Fig. 4.

20) R. Arnz, J. W. M. Carneiro, W. Klug, H. Schmickler, E. Vogel, R. Breuckmann, and F. Klärner, *Angew. Chem., Int. Ed. Engl.*, **30**, 683 (1991); E. Vogel, *Pure Appl. Chem.*,

65, 143 (1993).

21) If one assumes steric compression effects, the δ= 146.91 ppm signal may be assigned to be the C_3 carbon.

22) K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith, III, J. P. McCauley, D. R. Jones, Jr., and R. T. Gallagher. *J. Am. Chem. Soc.*, **114**, 1102 (1992).

23) Some black material insoluble in toluene also formed.

24) S. Yamago, H. Tokuyama, E. Nakamura, M. Prato, and F. Wudl, *J. Org. Chem.*, **58**, 4796 (1993).

25) Analytical samples were obtained by purification on the GPC HPLC using $CHCl_3$ as eluant, which was always included in the purified products. The content of $CHCl_3$ determined by elemental analysis was confirmed by ^{1}H NMR analysis of solution of the analytical sample.

26) R. E. Haufle, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanagan, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, W. E. Billups, M. A. Ciufoliui, J. L. Margrave, L. T. Wilson, R. F. Curl, and R. E. Smalley, *J. Phys. Chem.*, **94**, 8634 (1990).

27) W. A. Scrivens, P. V. Bedworth, and J. M. Tour, *J. Am. Chem. Soc.*, **114**, 7917 (1992).