Photochemical Synthesis, Conformational Analysis, and Transformation of [60]Fullerene−*o*-quinodimethane Adducts Bearing a Hydroxy Group

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The photochemical reactions of [60]fullerene with various aromatic aldehydes or ketones **1a**−**n** carrying an alkyl group at the ortho position were examined. Some of them afforded stable *o*-quinodimethane adducts **2** with a hydroxy group attached to the cyclohexene ring. The adducts **2** were found to adopt one or both of two conformers **A** and **E**, which possess pseudoaxial and pseudoequatorial hydroxy groups, respectively. The conformer ratios depended remarkably on the substituents attached to the aromatic nucleus and the cyclohexene ring. The dynamic behavior of **2** was also investigated by the VT-NMR technique.

Introduction

Among the functionalizations of [60]fullerene, Diels−Alder reactions with *o*-quinodimethanes as dienes are very versatile because they provide thermally stable adducts that are usually not subjected to cycloreversion into their original components.[1−6] The high stability is provided by the aromatic system generated in the adducts. *o*-Quinodimethane derivatives have been obtained as reactive intermediates, mainly from the thermolysis of benzocyclobutenes, the SO_2 extrusion of sulfolenes or sultines, or the iodide-induced 1,4 elimination of 1,2-bis(bromomethyl)benzene derivatives.[7] These precursors, however, are not necessarily easily available. Furthermore, the generation of *o*-quinodimethane from benzocyclobutenes requires rather high temperatures, which can lead to undesirable side reactions. In the iodide-induced 1,4 eliminations of α,α′-dihalides, appropriate phase-transfer catalysts such as 18-crown-6 are necessary in addition to iodide sources because [60]fullerene is almost insoluble in many polar organic solvents such as DMF.

The photoirradiation of *o*-tolualdehyde (**1a**) and related carbonyl compounds is known to give an *o*-quinodimethane species carrying a hydroxy group via the biradical generated by the intramolecular hydrogen abstraction of the carbonyl group in the excited triplet state (n−π*) from the neighboring methyl group.[8] *o*-Quinodimethane readily reacts with dienophiles, though it partially reverts to the starting material. Hence, in principle, it seems possible to obtain [60]fullerene−*o*-quinodimethane adducts by using [60]fullerene as a dienophile. However, it is rather difficult to efficiently produce the photoexcited states of aromatic carbonyl compounds in the presence of [60]-fullerene because the latter has stronger absorption bands throughout most of the UV region. For this reason, many of the known photochemical reactions involving [60]fullerene have taken advantage of the excited triplet state of [60]fullerene formed by intersystem crossing from the singlet excited state.[9]

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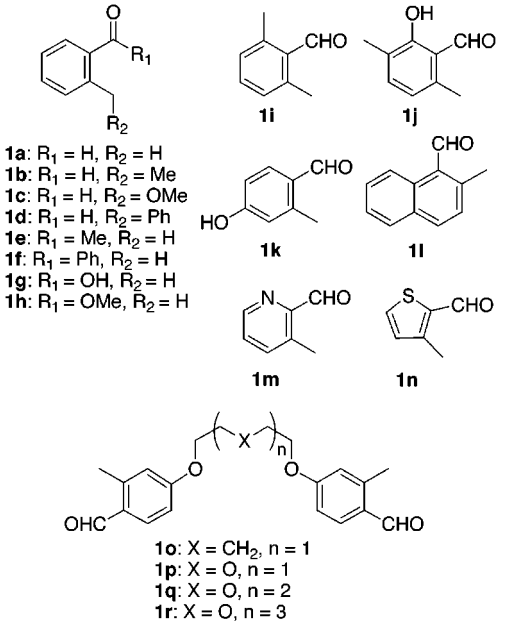
Chart 1

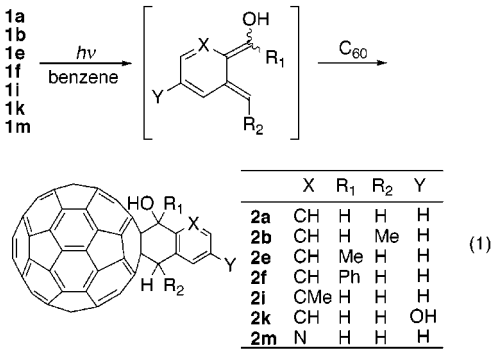


In this context, Tomioka et al. have examined the photoreaction of *o*-methylbenzophenone (**1f**) with [60]-fullerene.[10] Unexpectedly, the desired adduct **2f** was so unstable that they isolated only the monoalkyl-1,2-dihydrofullerene by the cleavage of the C−C bond connected to the fullerene core. In contrast, we have recently found that **1a** and several related compounds afford sufficiently stable [60]fullerene adducts.[11] This reaction is expected to be a useful method for preparing [60]-fullerene−*o*-quinodimethane adducts. Thus, we have further examined the reactions with various aromatic carbonyl compounds carrying an alkyl group at the ortho position. Here we report the versatility of this reaction, the substituent effects on the reactivity and conformational behavior, and further functionalization of the resulting adducts in detail.

Results and Discussion

Photoreactions Between [60]Fullerene and 1a−n. The photoreactions of [60]fullerene with **1a**−**n**, shown in Chart 1, were examined. The photoreaction with **1f** and the isolation of the resulting adduct were also reexamined.

A 1:1 mixture of [60]fullerene and **1a**−**n** in benzene (5×10^{-4} M) was irradiated with a 400 W high-pressure mercury lamp in a Pyrex vessel with stirring at room temperature for 6 h. These irradiation conditions can produce the excited species of **1a**−**n** as well as [60]-fullerene, though the latter is predominantly already in the excited state (e.g., the molar extinction coefficients (ϵ) of **1a** and [60]fullerene are 1×10^2 and 2×10^4 at 313 nm, respectively). Among them, **1a**, **b**, **e**, **f**, **i**, **k**, and **m** gave the desired monoadducts **2** along with the recovered [60]fullerene and a small amount of bisadducts (eq 1).



	X	R_1	R_2	Y
2a	CH	H	H	H
2b	CH	H	Me	H
2e	CH	Me	H	H
2f	CH	Ph	H	H
2i	CMe	H	H	H
2k	CH	H	H	OH
2m	N	H	H	H

(1)

The results of the photoreactions are summarized in Table 1.

o-Tolualdehyde (**1a**: $R_1 = R_2 = H$) and *o*-ethylbenzaldehyde (**1b**: $R_1 = H$, $R_2 = Me$) afforded the corresponding *o*-quinodimethane monoadducts **2a** and **b**, respectively. **2a** had been already prepared from benzocyclobutenol as a precursor of hydroxy-*o*-quinodimethane by Foote et al.[3] It is noteworthy that **2a** can be obtained from commercially available **1a** in a single step. Although the isolated yield listed here (32%) is lower than that obtained by the reported method (59%),[3] the yield based on the consumed [60]fullerene amounts to 87%. The irradiation of [60]fullerene was also investigated in the presence of excess **1a**. The yields of **2a** and bisadducts are listed in Table 2, along with the recovered [60]-fullerene yield. With increasing amounts of **1a** relative to the amount of [60]fullerene, the isolated yields of **2a** and bisadducts gradually increased, and the recovery of [60]fullerene decreased. The highest yield of **2a** was obtained for **1a**/[60]fullerene = 5:1. Using 9 equiv of **1a**, the yield of **2a** decreased while that of the bisadducts further increased. The decreased yield of **2a** under this condition is ascribed to the formation of products with higher polarity, probably trisadducts, in addition to the formation of bisadducts. These results suggest that the reactivity of **2a** with **1a** is comparable to that of [60]-fullerene itself because the bisadditions should proceed stepwise. The formation of bisadducts was confirmed by mass spectrometry. Their ^{1}H NMR spectra, however, indicated the formation of complex mixtures of regioisomers and stereoisomers, which were not subjected to further purification.

In attempting to accomplish regioselective bisaddition, we have also examined the reactions using precursors **1o**−**r** containing two *o*-tolualdehyde moieties tethered by oligomethylene or oligooxyethylene linkages of various lengths. Generally, covalent linkages between two reactive species effectively regulates their arrangement and distance and enhances regioselectivity in bisaddition, as demonstrated by several research groups.[12] However, there has so far been no example of the application of this technique to photochemical reactions. The photoirradiation of **1o**−**r** and [60]fullerene in benzene under conditions similar to those mentioned above produced one *o*-quinodimethane species that reacted with [60]fullerene to yield monoaddition products **2o**−**r** bearing an *o*-tolualdehyde moiety intact. Even by further irradiation of **2o**−**r**, the remaining *o*-tolualdehyde moiety was unchanged, and thus no desired bisadducts were obtained. Because the intermolecular reaction between [60]fullerene

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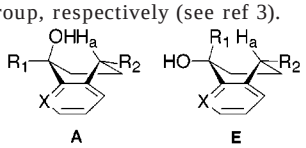
Table 1. Photoreaction of [60]Fullerene with 1

	precursor						conformer
	X	R_1	R_2	Y	adduct	yield/%[a]	ratio (**A**/**E**)[b]
1a	CH	H	H	H	2a	32 (63)	4:6
1b	CH	H	Me	H	2b	17 (80)	0:10[c]
1e	CH	Me	H	H	2e	9 (87)	6:4
1f	CH	Ph	H	H	2f	29[d] (69)	6:4
1i	CMe	H	H	H	2i	33 (58)	10:0
1k	CH	H	H	OH	2k	5 (89)	5.5:4.5
1m	N	H	H	H	2m	15 (83)	0:10

[a] Isolated yields are shown, although not optimized. Recovery of [60]fullerene is also shown in parentheses. [b] The symbols **A** and **E** denote conformers possessing a pseudoaxial and a pseudoequatorial hydroxy group, respectively (see ref 3).



A E

[c] Only a single conformer was obtained in which both the hydroxy and methyl groups adopt pseudoequatorial conformations. [d] A trace amount of the decomposition product is included.

Table 2. Reactions of [60]Fullerene with 1a under Various Conditions

	isolated yields/%		
molar ratio of **1a**/[60]fullerene	monoadduct **2a**	bisadduct	recovery of [60]fullerene/%
1	32	trace	63
3	40	8	32
5	45	16	20
9	18	20	7

and **1a** undoubtedly gave bisadducts, **2o**−**r** should have had sufficient reactivity for further photoreaction. The bridging linkage used here, especially that in **1q** or **r**, seems sufficiently flexible so that it is unlikely to prevent the second addition because of steric hindrance. Thus, the failure of the second *o*-tolualdehyde moiety to react with [60]fullerene is interpreted as follows: The irradiation of the monoadduct can produce the excited states of the second *o*-tolualdehyde moiety, as in the case of the first addition step. However, these excited states appear to decay rapidly because of the intramolecular energy transfer to the [60]fullerene moiety because the *o*-tolualdehyde moiety is located relatively close to the fullerene surface, in contrast to the intermolecular reaction between **2a** and **1a**. Hence, no intramolecular hydrogen abstraction that is necessary for the generation of *o*-quinodimethane takes place. The photoirradiation of **1o**−**r** and [60]fullerene under the present conditions also failed to give compounds carrying two [60]fullerene moieties that reacted with both ends of **1o**−**r**.

o-(Methoxymethyl)benzaldehyde **1c** (R_1 = H, R_2 = OMe) yielded a product whose UV−vis spectrum indicated a peak around 430 nm, which is characteristic of [60]fullerene monoadducts. The ^{1}H NMR spectra, however, were apparently inconsistent with the desired *o*-quinodimethane adducts; there were no suitable cyclohexene proton peaks. The identification of the products has been so far unsuccessful. The irradiation of **1d** (R_1 = H, R_2 = Ph) resulted in the recovery of [60]fullerene.

o-Methylacetophenone (**1e**) and *o*-methylbenzophenone (**1f**) also produced the desired monoadducts, though the yield using **1e** was rather low. In contrast, no desired adducts were formed from *o*-toluic acid (**1g**) and its methyl ester (**1h**).

The effects of the substituents directly attached to the benzene ring were also examined. 2,6-Dimethylbenzaldehyde (**1i**) gave adduct **2i**, while **1j**, bearing a hydroxy group at the ortho position of the formyl group, led to the recovery of [60]fullerene. In the excited state of **1j**, the proton transfer from the hydroxyl group to the carbonyl group must be predominant, thus preventing the hydrogen abstraction from the methyl group.[13] In contrast, **1k**, carrying a hydroxy group at the para position of the formyl group, successfully afforded **2k**, though the yield was extremely low.

The irradiation of aldehydes consisting of polycyclic aromatic or heteroaromatic rings was also examined. 2-Methyl-1-naphthaldehyde (**1l**) failed to give the desired monoadduct. In aromatic aldehydes containing larger π systems, the excited triplet state has $\pi-\pi^*$ character;[14] this state cannot be involved in the hydrogen abstraction. Intriguingly, monoadduct **2m** was obtained from **1m**, which has a pyridine ring, whereas only [60]fullerene was recovered from **1n**, which has a thiophene ring.

The obtained monoadducts, except for **2f**, were easily isolated as stable products by column chromatography (silica gel), and no decomposition products were detected. The purification of adducts is much easier than that in the reactions using benzocyclobutenes or 1,2-bis(bromomethyl)benzene derivatives as *o*-quinodimethane precursors. In contrast, the isolation of **2f** has been unsuccessful, although **2f** was a major product; a trace amount (ca. 1−2%) of the monoalkyl 1,2-dihydrofullerene reported in the literature[10] was not completely removed, despite several attempts to isolate **2f**, including recrystallization, HPLC, and GPC. Because this product was absent immediately after the photoirradiation, it was apparently formed during the purification process of **2f**.

To clarify the reactive species involved in the photoreaction, a mixture of [60]fullerene and **1a** was irradiated at 532 nm by using an Nd:YAG laser, in which [60]fullerene can be exclusively photoexcited. Under these irradiation conditions, intact [60]fullerene was recovered without the formation of desired adducts. This observation apparently demonstrates that these photoreactions require the excited states of carbonyl compounds, which generate *o*-quinodimethane by intramolecular hydrogen abstraction; the excited triplet state of [60]fullerene does not react with the ground state **1a** but decays back to the ground state.

Considering the extremely small absorbance of carbonyl compounds such as **1a** relative to that of [60]fullerene in the UV, it is noteworthy that the desired *o*-quinodimethane adducts were obtained by irradiation with a high-pressure mercury lamp in the presence of [60]fullerene. The successful progress of this reaction indicates that the *o*-quinodimethane is quite efficiently formed from the excited triplet state of carbonyl compounds and, subsequently, undergoes the Diels−Alder reaction with [60]fullerene sufficiently fast within their lifetimes. The high efficiency of these processes should enable the seemingly unfavorable reaction, where the incident light is only slightly absorbed by the component (e.g., **1a**) that needs to be photoexcited.

Structural Analysis of Monoadducts. The monoadducts obtained here were characterized by MS, UV, and NMR spectroscopy. **2a**, **b**, **e**, **f**, **i**, **k**, and **m** had molecular ion peaks corresponding to the desired monoadducts in

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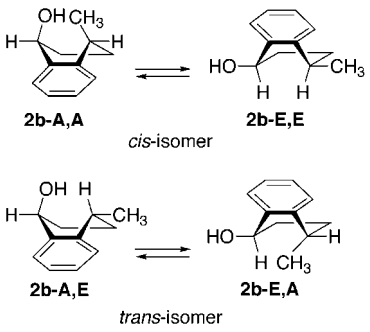
Table 3. Chemical Shifts (δ) of Cyclohexene-Ring Protons[a]

conformer	compound	OH	R_1	H_a	R_2
A	**2a**[b]	3.14	6.37 (H)	5.62	4.37 (H)
	2e	2.84	2.71 (Me)	5.85	4.35 (H)
	2f	3.12	(Ph)[c]	5.85	4.56 (H)
	2i	3.09	6.71 (H)	5.61	4.32 (H)
	2k	3.12	6.32 (H)	5.57	4.28 (H)
E	**2a**[b]	3.27	6.51 (H)	4.82	4.51 (H)
	2b	3.27	6.56 (H)	4.66	2.31 (Me)
	2e	3.01	2.62 (Me)	5.08	4.50 (H)
	2f	3.41	(Ph)[c]	5.04	4.26 (H)
	2k	3.26	6.45 (H)	4.76	4.40 (H)
	2m	5.81	6.45 (H)	4.86	4.53 (H)

[a] See Table 1 for each designation. [b] These values agree with those in reference 3. [c] Complex spectral patterns are observed.

Scheme 1

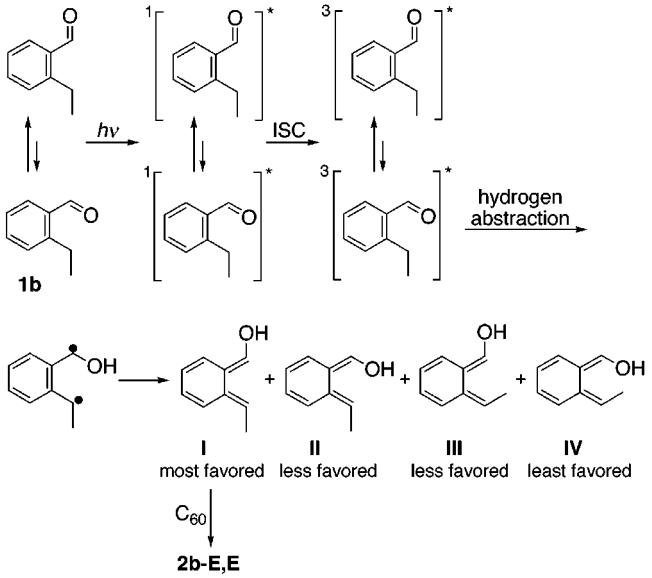


the FAB−MS spectra. Their UV−vis spectra were substantially identical to each other, despite the difference in substituents. All of these monoadducts displayed a sharp band around 430 nm and a weak band around 700 nm. These bands are characteristic of [60]fullerene monoadducts.[1,2] ^{1}H NMR spectra provided the most decisive information on the structure and conformation of adducts. The chemical shifts of cyclohexene-ring protons are listed in Table 3.

As reported by Foote et al.,[3] **2a** is composed of two conformers **2a-A** and **2a-E** possessing a pseudoaxial and a pseudoequatorial hydroxy group, respectively, that slowly exchange on the NMR time scale at room temperature. The conformer ratio **A**/**E** was 6:4, which is approximately in agreement with that reported in the literature.[3]

Adduct **2b** obtained from **1b** carries another substituent on the cyclohexene ring. Therefore, two diastereoisomers, cis and trans isomers, are possible for **2b**, each of which can be composed of two conformers, as shown in Scheme 1. Intriguingly, the ^{1}H NMR spectrum of **2b** indicated the existence of a single conformer of one diastereoisomer. Its stereochemistry was readily determined on the basis of NOE experiments. Because NOE interaction was observed between the two protons directly attached to the cyclohexene ring, the hydroxy and methyl groups were both assigned as pseudoequatorial (**2b-E,E**). This assignment is also supported by the similarity of chemical shifts of the cyclohexene and OH protons in **2b** to those in **2a-E** rather than to those in **2a-A** (Table 3). The absence of the trans isomer (**2b-E,A** or **2b-A,E**) and conformer **2b-A,A** of the cis isomer is apparently related to the stereochemistry of reaction intermediates generated from **2b**. As described above, the intramolecular hydrogen abstraction of **2b** affords an *o*-quinodimethane species with a hydroxy group (i.e., dienol) via quite a short-lived biradical.[6] The resulting

Scheme 2



dienol, for which four isomers **I**−**IV** are possible, undergoes a Diels−Alder reaction with [60]fullerene to give **2b** (Scheme 2). Among them, (*Z*)-dienols **II** and **IV** are known to revert rapidly to the original aldehyde via a [1,5]-sigmatropic hydrogen shift.[15] Of (*E*)-dienols **I** and **III**, **I**, which can lead to **2b-E,E**, appears to be more stable than **II** because of less steric hindrance. The PM3 calculations suggest that **I** is more stable than **III** by 3.0 kcal/mol. Such relative stability results in the exclusive formation of **2b-E,E**, which is unlikely to convert into **2b-A,A** because of the flagpole steric hindrance, thus resulting in the observation of the single conformer.

The ^{1}H NMR spectra of both **2e** and **f** indicated the existence of two conformers similar to **2a**, although an inseparable decomposition product was also involved in **2f**, as described above. The assignment of each conformer was established by comparison with the chemical shifts of **2a**; in conformer **E**, the hydroxy proton resonates at a lower field than it does in conformer **A**, while the H_a proton resonates at a higher field. On the basis of these observations, the major conformers for **2e** and **f** were assigned as **A**, which possesses a pseudoaxial hydroxy group, in contrast to that of **2a**. The conformer ratio **A**/**E** was 6:4 for both **2e** and **f**. The decrease in the ratio of **E** in **2e** and **f** relative to that of **2a** seems to result from the destabilization of **E** caused by the steric hindrance between the H_a proton and the R_1 (methyl or phenyl) group.

The interconversion between conformers **E** and **A** in **2e** was investigated by the variable-temperature (VT) NMR technique. Foote et al. estimated the $\Delta G^{\ddagger}$ value for **2a** to be 17.6 kcal/mol.[3] This value is much larger than that for the [60]fullerene−*o*-quinodimethane adduct with no hydroxy group on the cyclohexene ring (15.2 kcal/mol).[1b] The higher barrier for **2a** is attributable to the presence of the hydroxy group, which should destabilize the transition state and make the inversion difficult. In **2e** bearing two geminal substituents, the methyl group coalesced at 120 °C in $Cl_2CDCDCl_2$, whereas two sets of cyclohexene protons H_a and R_2 did not coalesce even at this temperature, though there was slightly broadening

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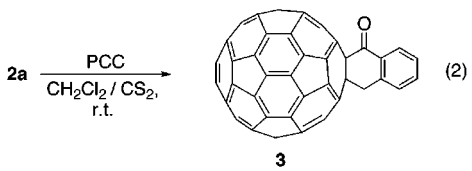
with increasing temperature. On the basis of the coalescence temperature of the methyl group, the $\Delta G^{\ddagger}$ value was estimated to be 19.6 kcal/mol. It is apparent that the additional methyl group further prevents the ring inversion relative to **2a**.

The ^{1}H NMR spectrum of **2m** produced from **1m** showed a single conformer that was similar to **2b**. This result is in remarkable contrast to **2a**, which consists of two conformers. On the basis of NOE experiments, the hydroxy group was found to adopt a pseudoequatorial conformation similar to that of **2b**; NOE interaction was observed between the R_1 and H_a protons. The addition of trifluoroacetic acid to **2m** induced considerable low-field shifts in the ^{1}H NMR spectrum, especially for the pyridine protons, indicating the protonation at the nitrogen atom, while only conformer **E** was still observed. These results suggest that the hydrogen bonding between the pyridine nitrogen atom and the hydroxy group is not responsible for the exclusive presence of conformer **E** in **2m**. The preference for **E** is probably ascribable to less steric interaction between the hydroxy group and the pyridine nitrogen atom than that found in **2a-E**, which possesses a phenyl C−H proton. This steric interaction was clearly demonstrated by the structural analysis of **2i**. Intriguingly, **2i** was composed of a single conformer, which was assigned as **A** on the basis of the comparison with the ^{1}H NMR spectral data of **2a**; the chemical shifts of the OH, H_a, and R_2 protons are comparable to those of **2a-A** rather than to those of **2a-E** (Table 3). The difference in the conformer ratios among **2a**, **2m**, and **2i** is remarkable; **2m** adopts only **E**, **2a**, both **A** and **E** (4:6), and **2i**, only **A**. These differences apparently correspond to the bulkiness of the X site of the aromatic ring; the value of **A**/**E** increases in the order X = N < CH < CCH_3.

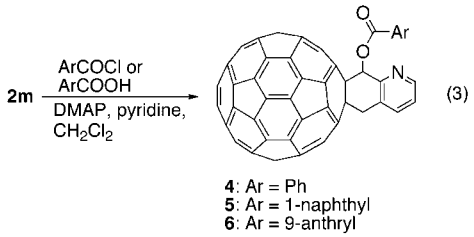
In **2k**, two conformers **A** and **E** were observed and were similar to those of **2a**. However, **A** was slightly predominant over **E** (**A**/**E** = 55:45), in contrast to the value of **A**/**E** for **2a**. The relatively high stability of conformer **A** in **2k** seems to be ascribed to some electronic effects of the hydroxy group that is attached to the benzene ring because this substituent is unlikely to affect sterically the relative stability of the two conformers.

Functionalization of Adducts Obtained. The hydroxy group of the monoadducts that were obtained is available for further functionalizations, which can alter the conformational behavior and also provide the adducts with additional properties.

First, we have examined the oxidation of **2a**, which should transform two conformers into a single entity. **2a** was allowed to react with excess PCC in CH_2Cl_2/CS_2 (1:1) at room temperature for 3 h to give the desired product **3**[16] (eq 2). In the ^{1}H NMR spectrum of **3**, the two cyclohexene protons were observed at δ 4.82 as a sharp singlet, indicating that the inversion is sufficiently fast on the NMR time scale, in contrast with that of **2a**. Such fast inversion was also demonstrated by the ^{13}C NMR spectrum showing C_s symmetry.



The conversion of the hydroxy group of **2a** into an ether or an ester group was investigated by Foote et al.[3] We have examined the *o*-acylation of **2m** bearing a pyridine residue and have prepared **4**, **5**, and **6** with a phenyl, a 1-naphthyl, and a 9-anthryl group, respectively (eq 3).



The *o*-acylation of **2m** with benzoyl chloride and 1-naphthoyl chloride was carried out in the presence of 4-(dimethylamino)pyridine (DMAP) and pyridine in CH_2Cl_2, in a manner similar to that reported by Foote et al.,[3] to yield esters **4** and **5**, respectively. For the preparation of **6**, **2m** was allowed to react with 9-anthroic acid in the presence of DCC and DMAP in toluene. **4**, **5**, and **6** are composed of two conformers each, in contrast to **2m**. The introduction of acyl groups into the hydroxy group of **2m** increases the steric interaction with the pyridine nitrogen atom, leading to the destabilization of conformer **E** relative to that of **A**. In each of **4**−**6**, the conformer ratio **A**/**E** was estimated to be approximately 1:1. The dynamic behavior of **A** and **E** was examined by VT-NMR in $Cl_2CDCDCl_2$ in a manner similar to that used with **2e**. Unfortunately, the coalescence of singlet peaks for the cyclohexene methine (R_1) proton was not clearly observed because they overlapped with the signals of some of the aromatic protons. Instead, the pyridine α-protons were found to coalesce at 70 °C for both **4** and **5** and at 60 °C for **6**. On the basis of these temperatures, the $\Delta G^{\ddagger}$ values for **4**, **5**, and **6** were estimated to be 17.2, 17.1, and 16.8 kcal/mol, respectively. These values are comparable to that for **2a** (Table 4). The difference in the aromatic nuclei was not so significantly reflected in the $\Delta G^{\ddagger}$ values.

Table 4. Activation Free Energies ($\Delta G^{\ddagger}$) for Ring Inversion in Adducts

adduct	$\Delta G^{\ddagger}$/kcal mol^{-1}
2a	17.6 ± 0.3[a]
2e	19.6 ± 0.3
4	17.2 ± 0.3
5	17.1 ± 0.3
6	16.8 ± 0.3

[a] Reference 3.

Summary

Stable *o*-quinodimethane adducts **2a**, **b**, **e**, **i**, **k**, and **m** possessing a hydroxy group that is applicable to further transformations were obtained from photochemical reactions between the corresponding carbonyl compounds and [60]fullerene. **A** and **E** conformers existed for **2a**, **e**, and **k**, while **2b**, **i**, and **m** exclusively adopted **E**, **A**, and **E** conformations, respectively. The conformer ratios were mainly dependent on the bulkiness of the substituents attached to the aromatic or cyclohexene ring, as clearly demonstrated by **2a**, **i**, and **m**. **2m**, bearing a pyridine ring, was successfully transformed into esters **4**−**6**, which adopted two conformations.

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Experimental Section

General. NMR spectra were recorded on a JEOL α-500 FT-NMR spectrometer with tetramethylsilane as an internal standard. FAB and APCI mass spectra were taken by a JEOL JMS-HX110A and a Shimadzu LC−MS QP-8000 mass spectrometer, respectively. Absorption spectra were recorded on a Hitachi U3210 spectrophotometer. Carbonyl compounds **1a**, **e**−**i**, and **n** were commercially available, whereas **1b**,[17] **c**,[18] **d**,[8a] **l**,[19] and **m**[20] were prepared by the lithiation of the corresponding bromides with *n*-butyllithium, followed by treatment with DMF.[21] **1j**[22] and **k**[23] were prepared by the formylation of 2,5-dimethylphenol and *m*-cresol, respectively, with dichloromethyl methyl ether and $TiCl_4$.

General Procedure for the Photoreaction of [60]-Fullerene and Carbonyl Compounds. A mixture of carbonyl compound **1b** (33.5 mg, 0.25 mmol) and [60]fullerene (180 mg, 0.25 mmol) in benzene (500 mL) was irradiated with a 400 W high-pressure mercury lamp in a Pyrex vessel at room temperature for 6 h. The reaction mixture was chromatographed on silica gel (toluene/hexane 4:1) to give unreacted [60]fullerene, monoadduct **2b**, and bisadducts. **2b** was obtained as brown powder (36 mg, 17%). The reaction also proceeded under sunlight.

Spectroscopic data of **2b**, **e**, **f**, **i**, **k**, and **m** are as follows. **2b**: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.95 (1H, d, J = 6.1 Hz), 7.70−7.60 (3H, m), 6.56 (1H, d, J = 7.0 Hz), 4.66 (1H, q, J = 6.7 Hz), 3.27 (1H, d, J = 7.0 Hz, OH), 2.31 (3H, d, J = 6.7 Hz); FAB MS m/z 854 (M^+).

2e: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) **2e-A** δ 7.85 (1H, d, J = 7.5 Hz), 7.70−7.54 (3H, m), 5.85 (1H, d, J = 13.8 Hz), 4.35 (1H, d, J = 13.7 Hz), 2.84 (1H, s, OH), 2.71 (3H, s, CH_3). **2e-E** δ 8.05 (1H, d, J = 8.2 Hz), 7.70−7.54 (3H, m), 5.08 (1H, d, J = 15.0 Hz), 4.50 (1H, d, J = 14.9 Hz), 3.01 (1H, s, OH), 2.62 (3H, s, CH_3); FAB MS m/z 854 (M^+).

2f: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) **2f-A** δ 8.20−7.10 (9H, m), 5.85 (1H, d, J = 14.0 Hz), 4.56 (1H, d, J = 14.1 Hz), 3.12 (1H, s, OH). **2f-E** δ 8.20−7.10 (9H, m), 5.04 (1H, d, J = 14.3 Hz), 4.26 (1H, d, J = 13.7 Hz), 3.41 (1H, s, OH); FAB MS m/z 916 (M^+).

2i: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.54 (1H, d, J = 7.0 Hz), 7.50 (1H, d, J = 7.7 Hz), 7.39 (1H, d, J = 7.7 Hz), 6.71 (1H, s), 5.61 (1H, d, J = 13.4 Hz), 4.32 (1H, d, J = 13.8 Hz), 3.09 (1H, s, OH), 2.66 (3H, s, CH_3); FAB MS m/z 854 (M^+).

2k: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) **2k-A** δ 7.61 (1H, d, J = 7.9 Hz), 7.16 (1H, d, J = 2.4 Hz), 6.98 (1H, dd, J = 7.9, 2.3 Hz), 6.32 (1H, d, J = 1.8 Hz), 5.57 (1H, d, J = 13.7 Hz), 5.10 (1H, s, ArOH), 4.28 (1H, d, J = 13.8 Hz), 3.12 (1H, d, J = 1.8 Hz, aliphatic OH). **2k-E** δ 7.80 (1H, d, J = 8.2 Hz), 7.18 (1H, d, J = 2.1 Hz), 7.08 (1H, dd, J = 8.5, 2.1 Hz), 6.45 (1H, d, J = 7.0 Hz), 5.00 (1H, s, ArOH), 4.76 (1H, d, J = 14.0 Hz), 4.40 (1H, d, J = 14.3 Hz), 3.26 (1H, d, J = 7.0 Hz, aliphatic OH); FAB MS m/z 856 (M^+).

2m: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.82 (1H, d, J = 5.2 Hz), 8.06 (1H, d, J = 7.3 Hz), 7.61 (1H, m), 6.45 (1H, d, J = 4.6 Hz), 5.81 (1H, d, J = 4.9 Hz, OH), 4.86 (1H, d, J = 13.9 Hz), 4.53 (1H, d, J = 14.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.60, 156.30, 155.13, 154.37, 151.54, 148.78, 147.74, 147.68, 147.53, 147.48, 146.57, 146.50, 146.46, 146.31, 146.23, 146.17, 146.14, 145.84, 145.63, 145.57, 145.48, 145.43, 145.33, 145.26, 145.21, 144.85, 144.66, 144.47, 144.40, 143.11, 142.93, 142.62, 142.57, 142.39, 142.23, 142.08, 141.94, 141.90, 141.79, 141.69, 141.59, 141.57, 141.55, 140.27, 140.08, 139.84, 139.10, 135.86, 135.81, 135.72, 135.63, 135.15, 130.50, 123.94, 73.28 (CHOH), 71.31, 65.22 (C_{60} sp^3-C), 42.05 (CH_2); FAB MS m/z 841 (M^+).

Preparation of 3 by the Oxidation of 2a. A mixture of **2a** (84 mg, 0.10 mmol) and PCC (107 mg, 0.50 mmol) in CS_2/CH_2Cl_2 (20 mL) was stirred at room temperature for 3 h. The reaction mixture was chromatographed on silica gel (toluene/hexane (4:1)) to give ketone **3**[16] as a brown powder (51 mg, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12 (1H, d, J = 7.7 Hz), 7.84 (1H, t, J = 7.7 Hz), 7.74 (1H, t, J = 7.7 Hz), 7.69 (1H, d, J = 7.7 Hz), 4.82 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 193.50 (C═O), 155.41, 152.14, 147.67, 147.52, 147.21, 146.50, 146.26, 146.22, 145.68, 145.61, 145.47, 145.41, 144.89, 144.60, 144.57, 142.99, 142.69, 142.62, 142.29, 142.02, 141.79, 141.76, 141.60, 141.53, 140.45, 140.13, 137.91, 135.62, 135.29, 135.27, 134.46, 128.63, 128.29, 127.78, 63.30 (C_{60} sp^3-C), 43.98 (CH_2) (Some peaks are missing because of the overlap.); IR ν(C═O) 1689 cm^{-1}; FAB MS m/z 838 (M^+).

Preparation of Ester 4. A mixture of **2m** (42 mg, 0.050 mmol), benzoyl chloride (46.2 μL, 0.40 mmol), 4-(dimethylamino)pyridine (49 mg, 0.40 mmol), and pyridine (40.2 μL, 0.50 mmol) in CH_2Cl_2 (35 mL) was stirred at room temperature for 24 h. After the solvent was evaporated in vacuo, toluene (10 mL) and 4 N HCl/EtOAc (0.2 mL) were added to dissolve the solid residue, and the solution was stirred at room temperature for 30 min. The mixture was extracted with a mixed solvent of toluene and ethyl acetate (9:1 (v/v)) (3 times), dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (toluene) to give **4** as a brown powder (36 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) **4-A** δ 8.82 (1H, d, J = 4.6 Hz, pyridine α-proton), 8.29 (2H, d, J = 7.3 Hz), 8.01 (1H, d, J = 7.0 Hz, pyridine γ-proton), 7.84 (1H, s), 7.63−7.39 (4H, m, aromatic), 5.59 (1H, d, J = 14.0 Hz), 4.51 (1H, d, J = 14.0 Hz). **4-E** δ 8.71 (1H, d, J = 5.5 Hz, pyridine α-proton), 8.17 (2H, d, J = 7.3 Hz), 7.97 (1H, d, J = 7.3 Hz, pyridine γ-proton), 7.68 (1H, s), 7.63−7.39 (4H, m, aromatic), 5.00 (1H, d, J = 14.2 Hz), 4.58 (1H, d, J = 14.2 Hz); APCI MS m/z 945 (M^+).

Preparation of Ester 5. 5 was prepared in 70% yield (28 mg) by a procedure similar to that used for **4**, using **2m** (34 mg, 0.040 mmol), 1-naphthoyl chloride (48.0 μL, 0.40 mmol), 4-(dimethylamino)pyridine (39 mg, 0.32 mmol), and pyridine (32.2 μL, 0.40 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) **5-A** δ 9.10 (1H, d, J = 3.6 Hz), 8.86 (1H, d, J = 4.6 Hz, pyridine α-proton), 8.62 (1H, d, J = 6.7 Hz), 8.08−7.42 (7H, m, aromatic), 8.00 (1H, s), 5.59 (1H, d, J = 14.2 Hz), 4.49 (1H, d, J = 14.2 Hz). **5-E** δ 9.09 (1H, d, J = 3.7 Hz), 8.75 (1H, d, J = 4.6 Hz, pyridine α-proton), 8.50 (1H, d, J = 7.0 Hz), 8.08−7.42 (7H, m, aromatic), 7.81 (1H, s), 5.04 (1H, d, J = 14.2 Hz), 4.60 (1H, d, J = 14.2 Hz); APCI MS m/z 995 (M^+).

Preparation of Ester 6. A mixture of **2m** (84 mg, 0.10 mmol), 9-anthroic acid (67 mg, 0.30 mmol), DCC (62 mg, 0.30 mmol), and DMAP (12 mg, 0.10 mmol) was refluxed in dry toluene (50 mL) for 5 days. The reaction mixture was chromatographed on silica gel (toluene) and further purified by GPC (chloroform) to give **6** as a brown powder (49 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) **6-A** δ 5.25 (1H, d, J = 14.1 Hz), 4.29 (1H, d, J = 13.7 Hz). **6-E** δ 5.12 (1H, d, J = 14.1 Hz), 4.66 (1H, d, J = 13.7 Hz) (The peaks corresponding to the cyclohexene methine (R_1) proton and a total of 12 protons of the pyridine and anthracene moieties were observed in the region δ 9.0−7.4.); APCI MS m/z 1045 (M^+).

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