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Facile modification of [60]fullerene by photochemically generated hydroxy-*o*-quinodimethane derivatives

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Abstract

o-Quinodimethane derivatives generated by a simple photolysis of commercially available *o*-tolualdehyde and related compounds efficiently reacted with [60]fullerene to give stable adducts possessing a hydroxy group which is applicable to further functionalization. © 2000 Elsevier Science Ltd. All rights reserved.

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Among the functionalizations of [60]fullerene, the Diels–Alder reactions with an *o*-quinodimethane species are a versatile reaction, since they usually provide thermally stable adducts.[1–5] *o*-Quinodimethane derivatives have been obtained as reactive intermediates mainly from the thermolysis of benzocyclobutenes[1–3] or the iodide-induced 1,4-elimination of 1,2-bis(bromomethyl)benzene derivatives.[4,5] These precursors, however, are not necessarily easily available. Furthermore, the generation of *o*-quinodimethane from the former precursors requires a rather high temperature, which can lead to undesirable side reactions. The photoirradiation of *o*-tolualdehyde (**1a**) 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.[6] The produced *o*-quinodimethane species readily reacts with dienophiles, though partly reverting to the starting material. Thus, we were prompted to utilize [60]fullerene as a dienophile, since the reaction is expected to give [60]fullerene-*o*-quinodimethane adducts. Tomioka et al. have already examined the photoreaction of *o*-methylbenzophenone with [60]fullerene, but the resulting adduct was so unstable as to produce the monoalkyl-1,2-dihydrofullerene via the cleavage of the C–C bond connected to the fullerene core.[7] However, we have found that **1a** or several related compounds afford sufficiently stable adducts. Here we report the efficient formation of [60]fullerene-*o*-quinodimethane adducts from easily available precursors by a simple procedure.

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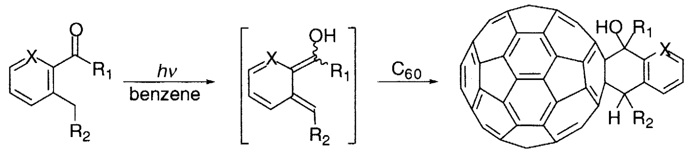


1a (X = CH, R1 = R2 = H)
1b (X = CH, R1 = H, R2 = Me)
1c (X = CH, R1 = Me, R2 = H)
1d (X = N, R1 = R2 = H)

2a (X = CH, R1 = R2 = H)
2b (X = CH, R1 = H, R2 = Me)
2c (X = CH, R1 = Me, R2 = H)
2d (X = N, R1 = R2 = H)

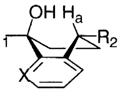
(1)

A 1:1 mixture of [60]fullerene and **1a**–**d** in benzene (5×10^{-4} M) was irradiated with a 400 W high-pressure mercury lamp in a Pyrex vessel at room temperature for 6 h. These irradiation conditions can produce the excited species of **1a**–**d** as well as [60]fullerene. In all cases, the desired monoadducts **2a**–**d** were obtained with a slight amount of bisadducts (Eq. (1)). Adducts **2a**–**d** were easily isolated as stable products by column chromatography (silica gel) and no decomposition products were detected. The results of the photoreactions are summarized in Table 1. All of **2a**–**d** indicated a molecular ion peak in the FAB-MS spectra and showed a sharp band around 430 nm characteristic of [60]fullerene monoadducts in the UV–vis spectra.[5]

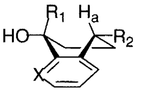
Table 1
Photoreaction of [60]fullerene with **1a**–**d**

Precursor	Adduct	Yield / %[a]	Conformer ratio (**A** : **E**)[b]
1a (X = CH, R_1=R_2=H)	**2a**	32 (63)	4 : 6
1b (X = CH, R_1=H, R_2=Me)	**2b**	17 (80)	0 : 10[c]
1c (X = CH, R_1=Me, R_2=H)	**2c**	9 (87)	6 : 4
1d (X = N, R_1=R_2=H)	**2d**	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 pseudoequatorial hydroxy group, respectively. [c] Only a single conformer was obtained, in which both the hydroxy and methyl groups adopt pseudoequatorial conformation.



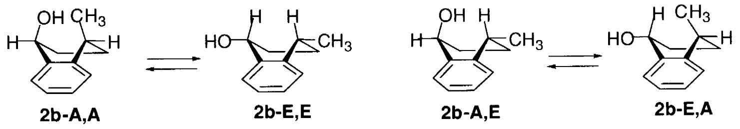
A



E

o-Tolualdehyde (**1a**) efficiently afforded adduct **2a** (32% yield), which had already been 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. Since the reaction conditions have not been optimized, the isolated yield listed here is lower than that by the reported method (59%),[3] but the yield based on the consumed [60]fullerene amounts to 87%. This adduct was found to be composed of two conformers **2a-A** and **2a-E** possessing a pseudoaxial and pseudoequatorial hydroxy group, respectively, slowly exchanging on the NMR time scale at room temperature, and the conformer ratio was approximately in agreement with that in the literature.[3]

o-Ethylbenzaldehyde (**1b**) also gave adduct **2b** carrying another substituent on the cyclohexene ring in 17% yield. As for **2b**, two diastereoisomers are possible, 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. Since the 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 fact that the chemical shifts of the cyclohexene and OH protons of **2b** are similar to those of **2a-E** rather than **2a-A** (Table 2). The absence of diastereoisomer **2b-E**,**A** (or **2b-A**,**E**) and conformer **2b-A**,**A** suggests that the intermediate *o*-quinodimethane species exclusively adopt the configuration leading to **2b-E**,**E**. The produced **2b-E**,**E** is unlikely to convert into **2b-A**,**A** due to the flagpole steric hindrance, thus resulting in the observation of the single conformer.



Scheme 1.

Table 2
Chemical shifts (δ) of cyclohexene-ring protons[a]

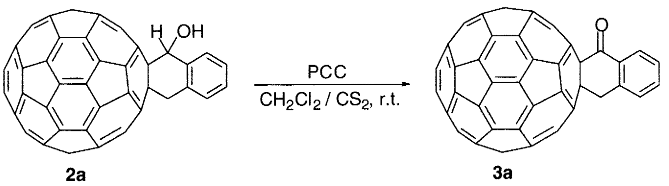
Conformer	Compound	OH	R_1	H_a	R_2
A	**2a**[b]	3.14	6.37 (H)	5.62	4.37 (H)
	2c	2.84	2.71 (Me)	5.85	4.35 (H)
E	**2a**[b]	3.27	6.51 (H)	4.82	4.51 (H)
	2b	3.27	6.56 (H)	4.66	2.31 (Me)
	2c	3.01	2.62 (Me)	5.08	4.50 (H)
	2d	5.81	6.45 (H)	4.86	4.53 (H)

[a] See Table 1 for each designation. [b] These values agree with those in Ref. 3.

The irradiation of **1c** resulted in the formation of **2c**. The ^{1}H NMR spectral pattern of **2c** is similar to that of **2a**, indicating that these adducts also consist of two conformers. The assignment of each conformer was accomplished by comparing the chemical shifts; the pseudoequatorial hydroxy group is resonated at lower fields than the pseudoaxial one due to the deshielding effect of the fullerene moiety. For **2c**, the major conformer is **A** possessing a pseudoaxial hydroxy group in contrast with **2a**.

3-Methyl-2-pyridinecarbaldehyde (**1d**) afforded **2d**, which was obtained as a single conformer. On the basis of NOE experiment, the hydroxy group was found to adopt pseudoequatorial conformation similar to **2b**. The reason for the absence of the conformer with a pseudoaxial hydroxy group has not been clarified at the present stage.

Aromatic aldehydes consisting of a larger π-system, such as 2-alkyl-1-naphthaldehyde, failed to give the corresponding adduct, probably because the excited triplet state has a π–π* character, which cannot be involved in the hydrogen abstraction.



(2)

We have examined the oxidation of **2a**, which should transform two conformers into a single one. Adduct **2a** was allowed to react with excessive PCC in CH_2Cl_2/CS_2 (1:1) at room temperature for 3 h to give the desired product **3a** quantitatively (Eq. (2)). In the ^{1}H NMR spectrum of **3a**,[8] 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 **2a**. Such fast inversion was also demonstrated by the ^{13}C NMR spectrum showing C_s symmetry.[8]

In summary, the photoirradiation of alkylbenzenes carrying an acetyl or formyl group at the *ortho*-position in the presence of [60]fullerene successfully affords stable hydroxy-*o*-quinodimethane adducts possessing a hydroxy group that is applicable to further transformations. This photoreaction appears to be a quite simple and versatile method for the functionalization of [60]fullerene. Further studies on the reaction mechanism are in progress.

Acknowledgements

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8. Selected spectroscopic data of **3a**. ^{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, 43.98 (some peaks are missing due to the overlap); IR ν(C=O) 1689 cm^{-1}; FAB-MS *m/z* 838 (M^+).