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NaOH-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes: Transition-Metal-Free, General, and Efficient Synthesis of Single-Bonded [60]Fullerene Dimers

Shirong Lu,[†,‡] Tienan Jin,[*,†] Ming Bao,[‡] and Yoshinori Yamamoto[†,‡]

WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan, and State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China

tjin@m.tohoku.ac.jp

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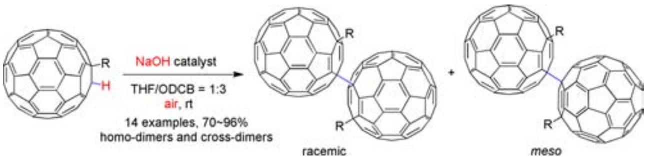
ABSTRACT



Unprecedented, transition-metal-free NaOH-catalyzed homo- and cross-dimerizations of monofunctionalized hydrofullerenes are reported. Various single-bonded fullerene dimers were synthesized under mild reaction conditions with remarkably high yields. The use of a NaOH catalyst combined with tetrahydrofuran as a cosolvent under an air atmosphere is critical in achieving highly efficient catalytic dimerization.

The single-bonded fullerene dimer $RC_{60}{-}C_{60}R$ with a direct covalent bond between two C_{60} cages has attracted much attention due to not only its potential interesting optical and electronic properties through the interaction of two adjacent fullerene cages[1] but also its useful functionalization ability as a monomer radical ($RC_{60}^{\bullet}$) precursor.[2] The pioneered experimental and theoretical studies on these fullerene dimers revealed that they consist of racemic and *meso* isomers which were usually formed by the dimerization of $RC_{60}^{\bullet}$.[3,4] Accordingly, in the past few years, versatile synthetic methods for the construction of the single-bonded fullerene dimers have been reported.[2−8] For example, the photoirradiation radical addition of C_{60} with perfluoroalkyl iodides in the presence of $(R_3Sn)_2$,[4a] $Mn(OAc)_3$-mediated radical reaction of C_{60} with phosphonate esters or dialkyl malonates,[4c,6] one-electron oxidation of the monoanion RC_{60}^{-} through an excess amount of oxidants,[2b,4b,5d,7] and electroreduction of 1,2-$(PhCH_2)$-HC_{60}[8] have been reported to form the single-bonded fullerene dimers. However, their wide application to the

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[†] Tohoku University.

[‡] Dalian University of Technology.

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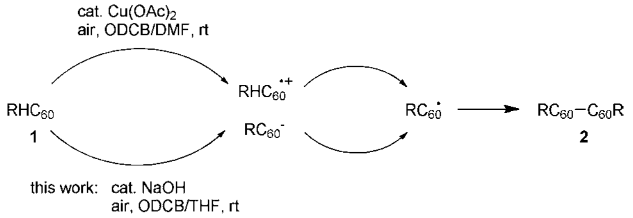
elaborated fullerene dimers generally suffered from the limited scope of functional groups, low chemical yields, harsh reaction conditions, and use of large excess amounts of toxic reagents or additives. Recent advances in the catalytic functionalization of fullerene[9] triggered us to explore the highly efficient catalytic dimerization of hydrofullerenes which may offer advantages such as high chemical yields and selectivity as well as high functional group compatibility under mild conditions.

Most recently, we found that the $Cu(OAc)_2$ catalyst combined with a small amount of DMF as a cosolvent under air was crucial for dramatic enhancement of the dimerization efficiency of monosubstituted hydrofullerenes (RHC_{60}) (**1**),[9m] affording the corresponding fullerene dimers **2** in high yields (Scheme 1).[10] The reaction most probably proceeds through the $Cu(OAc)_2$-catalyzed generation of a fullerenyl radical cation species ($RHC_{60}^{\bullet+}$) followed by formation of a fullerenyl monoradical $RC_{60}^{\bullet}$. However, the drawback of toxic copper contamination of the products and solvents may preclude its use in materials science and practical synthetic application.[11] Taking these points into consideration, we envisioned that by using the suitable, nontoxic base as a catalyst in the presence of air and cosolvent, the catalytic dimerization of RHC_{60} (**1**) should be accomplished through the generation of monoanion RC_{60}^{-} with base treatment followed by formation of $RC_{60}^{\bullet}$ by one-electron oxidation.[5d,12] Herein, we report unprecedented, efficient, and nontoxic NaOH-catalyzed homo- and cross-dimerizations of monofunctionalized hydrofullerenes **1** that afford the single-bonded fullerene dimers **2** as a mixture of racemic and *meso* isomers in excellent yields in the presence of air and tetrahydrofuran (THF) cosolvent under mild reaction conditions (Scheme 1). To the best of our knowledge, this is *the first example for transition-metal-free catalytic functionalization of fullerenes* which provides an alternative and promising method for catalytic dimerization of hydrofullerenes, meeting the requirements for both green chemistry and fullerene chemistry.

Scheme 1. $Cu(OAc)_2$- and NaOH-Catalyzed Dimerization of Hydrofullerenes **1** for Synthesis of Single-Bonded [60]Fullerene Dimers **2**



In the preliminary experiment, we found that the homodimerization of monosubstituted **1a** in the presence of an as-prepared NaOH (10 mol %) by using ODCB (*ortho*-dichlorobenzene) as a sole solvent in air at rt did not proceed, and **1a** was recovered almost quantitatively (Table 1, entry 1). The remarkable enhancement of efficiency by adding DMF or CH_3CN, which was reported by our previous $Cu(OAc)_2$-catalyzed dimerization,[10] led us to examine the notable cosolvent effect on the present dimerization. To our delight, addition of the polar cosolvents, such as DMF, THF, and CH_3CN, improved the yields of the corresponding dimer **2a** drastically to 89%, 95%, and 90%, respectively (entries 2−4), although we reported previously that the use of THF as a cosolvent combined with the $Cu(OAc)_2$ catalyst afforded only a 20% yield of **2a**.[10] Addition of less-coordinative cosolvents, such as toluene or chloroform, did not exert any influences on the reaction efficiency (entries 5 and 6). Previously, we also reported that the use of a catalytic or stoichiometric amount of $Cu(OAc)_2$ in the absence of air produced the corresponding dimer **2a** in 14% and 93% yields, respectively.[10] Interestingly, in sharp contrast to these results, the present NaOH-mediated dimerization did not afford the corresponding dimer **2a** with either a catalytic or stoichiometric amount of NaOH (entries 7 and 8). These results not only indicate that air play as an important role in the generation of monomer radical $RC_{60}^{\bullet}$ but also imply that the present NaOH-catalyzed dimerization might form $RC_{60}^{\bullet}$ in a completely different way from the $Cu(OAc)_2$-catalyzed reaction. To gain further insight into the role of bases, we examined various base catalysts. Strong inorganic bases, such as KOMe, KO^tBu, CsOH, and KOH, produced the corresponding fullerene dimer **2a** in high yields (entries 9−12), while other inorganic bases having a relatively lower basicity, such as LiOH and Na_2CO_3, are less active (entries 13 and 14). Strong organic base Me_4NOH produced **2a** in a short reaction time (2 h), but the yield was lower than that of NaOH (entry 15). The weaker organic base Et_3N showed low catalytic activity regardless of the prolonged reaction time (entry 16). It is clear that the reaction did not proceed without base catalysts (entry 17).

With the optimized reaction conditions in hand, various monosubstituted hydrofullerenes **1** were examined as shown in Table 2. A variety of functional groups in hydrofullerenes **1** were tolerated under the present NaOH-catalyzed dimerization conditions, affording the corresponding single-bonded fullerene dimers **2** in very high

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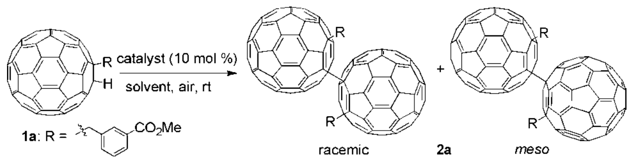
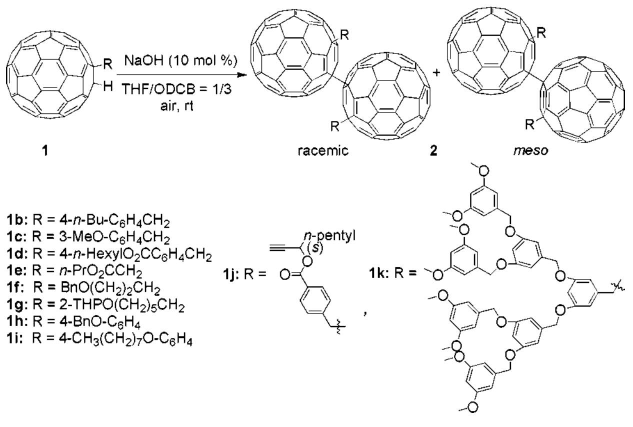
Table 1. Screening of Catalysts and Solvents for Homodimerization of Monofunctionalized [60]Hydrofullerenes[a]



entry	catalyst (1 M in H_2O)	solvent (1:3)	time (h)	**2a** (%)[b]	**1a** (%)[b]
1	NaOH	ODCB	12	trace	97
2	NaOH	DMF/ODCB	12	89	4
3	NaOH	THF/ODCB	12	95 (91)	0
4	NaOH	CH_3CN/ODCB	12	90	2
5	NaOH	Toluene/ODCB	20	trace	99
6	NaOH	$CHCl_3$/ODCB	20	0	99
7[c]	NaOH	THF/ODCB	12	trace	98
8[c,d]	NaOH	THF/ODCB	12	trace	97
9	KOMe	THF/ODCB	13	93	0
10	KO^{t}Bu[e]	THF/ODCB	13	92	1
11	CsOH	THF/ODCB	13	92	4
12	KOH	THF/ODCB	13	91	0
13	LiOH	THF/ODCB	20	31	63
14	Na_2CO_3	THF/ODCB	20	9	88
15	Me_4NOH	THF/ODCB	2	88	0
16	Et_3N	THF/ODCB	26	26	70
17	none	THF/ODCB	12	0	99

[a] Conditions: To a 1,2-dichlorobenzene (ODCB) (3 mL) and cosolvent (1 mL) of **1a** (0.03 mmol) under air atmosphere was added base catalyst (10 mol %, 1 M aqueous solution). The resulting mixture was stirred at rt for the times shown. [b] HPLC yields determined using C_{60} as an internal standard. Isolated yield by silica-gel chromatography is shown in parentheses. [c] Reaction was conducted under argon atmosphere. [d] 1.0 equiv of NaOH catalyst was used. [e] A THF solution was used.

Table 2. NaOH-Catalyzed Homodimerization of Monosubstituted Hydrofullerenes[a]



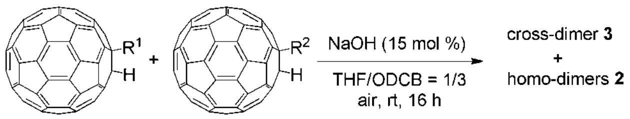
entry	**1**	time (h)	**2**	yield **2** (%)[b]
1	**1b**	13	**2b**	85
2[c]	**1c**	12	**2c**	93
3	**1d**	13	**2d**	90
4	**1e**	12	**2e**	86
5[c]	**1f**	20	**2f**	96
6[d]	**1g**	20	**2g**	91
7[c]	**1h**	20	**2h**	84
8[c]	**1i**	20	**2i**	79
9	**1j**	15	**2j**	94
10[c]	**1k**	14	**2k**	74

[a] Conditions: To a 1,2-dichlorobenzene (ODCB, 3 mL) solution of **1** (0.03 mmol) and THF (1 mL) under an air atmosphere was added NaOH (1 M in H_2O, 10 mol %, 3 μL). The resulting mixture was stirred at rt for the times shown. [b] Isolated yields. [c] 15 mol % NaOH was used. [d] 20 mol % NaOH was used.

yields. All of the reactions were monitored by TLC and HPLC analysis and the corresponding dimers **2** were purified by silica gel column chromatography as a mixture of *meso* and racemic isomers. 1,2-Benzyl(hydro)fullerenes bearing an *n*-butyl (**1b**) or a methoxy group (**1c**) on the benzene rings underwent the NaOH-catalyzed dimerization smoothly, affording the corresponding dimers **2b** and **2c** in high yields (entries 1 and 2). Remarkably, hydrofullerenes **1d**, **1e**, and **1j** having the base sensitive ester substituents were also tolerated, giving the expected dimers in high yields without any formation of the hydrolyzed byproducts (entries 3, 4, and 9). Alkyl- or aryl-substituted hydrofullerenes **1f**–**i** having benzyl-, THP-, and *n*-octyl-protected ethers are also active substrates, producing the corresponding dimers **2f**–**i** in high yields, whereas a large amount of catalytic loading is required (entries 5–8). The present NaOH-catalyzed dimerization was applied to the construction of a fullerene-bound dendrimer, which is expected to show some special electronic property arising from the fullerene cage and dendrimer moiety. Under the standard catalytic conditions, the fullerene-bound dendrimer **1k** afforded the corresponding dendritic dimer **2k** in 74% yield, which exhibited high solubility in various common organic solvents, such as THF, $CHCl_3$, and benzene (entry 10).

The present NaOH-catalyzed dimerization was also successfully applied to the synthesis of cross-dimers containing two different functionalized C_{60} units (Table 3). Under the standard reaction conditions, cross-dimerization of two different alkyl(hydro)fullerenes **1a** and **1g** occurred smoothly to produce the desired cross-dimer **3a** in 30% yield together with the two homodimers **2a** and **2g** in 24% and 29% yield, respectively (entry 1). It was noted that these three dimers were purified by flash silica gel chromatography. As we reported previously, cross-dimers **3** were speculated to consist of four isomers according to the four possible kinds of monoradicals,[10] although the individual isomers cannot be completely identified from ^{1}H NMR and HPLC analysis because they are difficult to separate through silica gel chromatography and HPLC. Similarly, the NaOH-catalyzed cross-dimerization of alkyl(hydro)fullerenes **1a** and **1f** as well as **1f** and **1g** also proceeded smoothly to afford the corresponding cross-dimers **3b** and **3c** in 34% and 33% yield, respectively, together with the corresponding homodimers (entries 2 and 3). The homodimers **2** are in equilibrium with cross-dimers **3** in solvent at rt that provides an alternative method for the synthesis of these promising cross-dimers **3** from various homodimers **2** through their interconversion in solution. It should be noted that both homo- and cross-dimers are very stable in the solid state; they can be stored for several months at ambient temperature without any decomposition.

Table 3. NaOH-Catalyzed Cross-Dimerization[a]

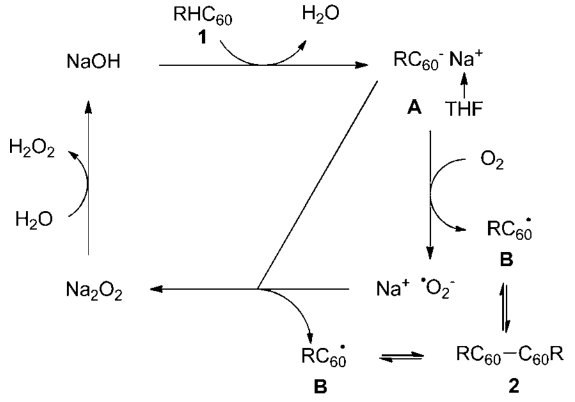


entry	**1** (R^1)	**1** (R^2)	homodimer **2** (%)[b]	cross-dimer **3** (%)[b]
1	**1a**	**1g**	24 (**2a**); 29 (**2g**)	30 (**3a**)
2	**1a**	**1f**	26 (**2a**); 28 (**2f**)	34 (**3b**)
3	**1f**	**1g**	29 (**2f**); 29 (**2g**)	33 (**3c**)

[a] Conditions: To a 1,2-dichlorobenzene (ODCB, 6 mL) solution of two different hydrofullerenes **1** (0.03 mmol) and THF (2 mL) under an air atmosphere was added NaOH (15 mol %, 1 M aqueous solution). The resulting mixture was stirred at rt for 16 h. [b] Dimers **2** and **3** were isolated by silica-gel chromatography.

A notable feature of an acidic C−H bond[13] in hydrofullerenes **1** and our experimental observations, as well as early works on base catalyzed dimerization of mercaptans,[12] led us to propose the monoanion oxidation mechanism as shown in Scheme 2.[14] Initially, deprotonation of an acidic proton in hydrofullerenes **1** by the strong base NaOH forms a fullerenyl monoanion sodium complex **A**, wherein a polar solvent such as THF may stabilize **A**. Indeed, when hydrofullerene **1a** was treated with a stoichiometric amount of NaOH in an argon atmosphere without air, the color of the reaction mixture was changed to dark green, indicating the generation of a monoanion species (Table 1, entry 8).[4b] One-electron oxidation of the monoanion sodium complex **A** by O_2 in air forms the monoradical **B** which produces the corresponding single-bonded fullerene dimers **2**.[4b,5b,5d,12] Moreover, we assume that further one-electron oxidation of monoanion **A** may take place by an *in situ* generated $^{\bullet}O_2^{-}$ oxidant, leading to monoradical **B**.[12a] Finally, hydrolysis of sodium peroxide regenerates the NaOH catalyst which enters into the next catalytic circle. Dimerization of two monoradicals having an *R* and *S* configuration produces the *meso* isomer (*R*-*S*), whereas dimerization of two monoradicals with the same configuration gives a racemic mixture of *R*-*R* and *S*-*S* isomers.[4c]

Scheme 2. A Plausible Mechanism for the NaOH-Catalyzed Dimerization of Monosubstituted Hydrofullerenes



In conclusion, we have developed unprecedented, transition-metal-free NaOH-catalyzed homo- and cross-dimerizations of monofunctionalized hydrofullerenes. The present novel catalytic dimerization provided a general, efficient, mild, and green method for the construction of various single-bonded fullerene dimers with remarkably high yields. Compared with our previous $Cu(OAc)_2$-catalyzed dimerization, the present NaOH catalysis avoided use of the toxic and expensive copper salts while retaining its high catalytic efficiency. The NaOH catalyst combined with a small amount of THF as a cosolvent in air is crucial for the efficient formation of the corresponding single-bonded fullerene dimers. Investigation on their chemical and electronic properties and application to materials science are in progress.

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Supporting Information Available. Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) An alternative reaction pathway, such as the generation of a fullerenol intermediate through hydroxylation of **1a**, is unlikely because, without any fullerenol, derivatives were observed from ^1H NMR and HPLC analysis under the standard reaction conditions and the reaction using H_2O_2 instead of air; the reaction of **1a** under aqueous basic conditions in the presence of H_2O_2 (50 equiv) in an argon atmosphere produced the corresponding dimer **2a** in 23% yield (8 h) together with a 72% yield of the recovered **1a**.

The authors declare no competing financial interest.