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#### LETTER

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#### Reaction of $C_{60}$ radical anion with alkyl halide $\dagger$

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Reaction of the  $C_{60}$  radical anion ( $C_{60}^{-1}$ ) with  $\alpha$ -bromo-1,3-dicarbonyl compounds selectively afforded methanofullerene derivatives. The reaction with benzyl halide and 1,2-bis(dihalomethyl)benzene afforded the corresponding 1,4-dibenzylated  $C_{60}$  derivative and cycloaddition product, respectively. Possible mechanisms for the formation of the fullerene adducts are proposed.

The functionalization of fullerenes has attracted a great deal of attention in disciplines such as material science, catalysis, and medical science. A large number of reactions have been developed in recent years to determine the chemical reactivity of fullerenes and to control their physical and chemical properties.<sup>1-7</sup> Activation of the fullerenes by chemical or electrochemical reduction is an effective method for their functionalization. Kadish et al. reported that an electrochemically generated  $C_{60}$  dianion ( $C_{60}^{2-}$ ) reacts with organic halides to afford the corresponding bis-adducts.<sup>8</sup> Chemical reduction to generate  $C_{60}^{2-}$  is advantageous for the activation of  $C_{60}$  because of its simple operation.9,10 These reductive alkylation reactions have been applied to the functionalization of endohedral metallofullerenes<sup>11,12</sup> and carbon nanotubes.<sup>13-15</sup> Recently, reactions utilizing the high oxidation reactivity of both  $C_{\rm 60}{}^{2\text{-}}$  and alkylated  $C_{\rm 60}$ anion species have been reported.<sup>16</sup> In addition, dihydrofuran-,<sup>17-21</sup> lactone-,  $^{22}$  and oxazoline-fused  $^{23}\ \mbox{C}_{60}$  can be synthesized from an alkylated  $C_{\rm 60}$  radical anion or an alkylated  $C_{\rm 60}$  radical anion having a β-carbonyl group.

In this communication, we report the reaction of  $C_{60}$ , with alkyl halides and alkyl dihalides (Scheme 1). It is well known that the  $C_{60}$  radical anion ( $C_{60}$ ) is an important intermediate in various electron transfer systems. To handle active  $C_{60}^{2-}$ , anaerobic conditions and highly polar solvents, such as acetonitrile and benzonitrile, are required. In contrast,  $C_{60}$ , has higher stability and easier handling. For

example,  $C_{60}$  and  $C_{60}$ <sup>-</sup> have sufficient solubility in 1,2dichlorobenzene (1,2-DCB) to allow the expansion of a flow reactor system. Understanding of the reactivity of  $C_{60}$ <sup>-</sup> also contributes to the understanding of metallofullerene and carbon nanotube chemistry.

In a typical experiment, 10 equiv of alkyl halide was added to a solution of  $C_{60}$  around 1.67 × 10<sup>-3</sup> M that had been generated by bulk electrolysis in 1,2-DCB containing 0.13 M tetrabutylammonium perchlorate (TBAP). The reaction was monitored by vis near-infrared (NIR) absorption spectroscopy to confirm the disappearance of the characteristic peaks of  $C_{60}$  at 1089 nm.<sup>24</sup> After the disappearance of the characteristic peak of  $C_{60}$ , 1,2-DCB was removed under reduced pressure and the reaction mixture was dissolved in carbon disulfide, then filtered to remove precipitated TBAP. The products were isolated either by preparative high-performance liquid chromatography (HPLC) using a Buckyprep column or by flash chromatography.

Scheme 1



The structures of the  $C_{60}$  derivatives were characterized using matrixassisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, NMR spectroscopy, and UV-vis NIR absorption spectroscopy. The spectral data of 2a,<sup>25</sup> 2b,<sup>26</sup> 2c,<sup>27</sup> 2e,<sup>28</sup> 4,<sup>29</sup> and  $6^{30}$ are consistent with previous reports. For example, the MALDI-TOF mass spectrum of 2a displayed a strong peak at m/z 878, corresponding to the mono adduct of  $C_{60}$  and 1a. The visible absorption spectrum of 2a showed an absorption maximum at 428 nm, which is characteristic of a 6,6-addition on  $C_{60}$ . The NMR spectra

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of **2a** displayed the proton signals of the ethyl groups at 1.48 and 4.52 ppm, as well as the carbon signals of the ethyl groups at 14.3 and 63.1 ppm. The <sup>13</sup>C NMR spectrum also showed one quaternary carbon peak corresponding to the sp<sup>3</sup> carbon atoms of C<sub>60</sub> at 71.5 ppm and one carbonyl carbon peak at 163.0 ppm. In addition, the <sup>13</sup>C NMR showed 13 peaks in the range of 139-145 ppm for the C<sub>60</sub> cage due to the overlapping of 3 peaks.

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59 60 As summarized in Table 1, the reaction of  $C_{60}$  is extended to  $\beta$ dicarbonyl compounds, such as a diester (entry 1), keto esters (entries 2 and 3), and  $\beta$ -diketones (entries 4 and 5), which afforded the corresponding methanofullerenes (**2a-2e**). The mono-adducts were selectively formed in high conversion yields based on the consumption of C<sub>60</sub>. The bis-adducts were separated in 4% yield as isomer mixtures from the reaction of C<sub>60</sub><sup>--</sup> with **1a**. The high recovery (39-63%) of C<sub>60</sub> as the neutral form suggests that two C<sub>60</sub><sup>--</sup> molecules were consumed for every methanofullerene molecule formed. The relatively low yield of **2e** might be because of reduced purification efficiency due to its low solubility.

# Table 1. The substrate equivalents and yields for the reaction of $C_{60}^{-}$ with 1, 3, and 5. Yields in parentheses are based on the amount of $C_{60}$ consumed.

Entry	Substrate	Equiv of substrate	Yield of C <sub>60</sub> derivatives (%)	Recovered C <sub>60</sub> (%)
1	EtO Br OEt	10	40 (77) 4 (7) (bis-addu	48 uct)
2	1a O O Br 1b	10	38 (80)	52
3	Ph Br 1c	10	42 (93)	55
4	O O Ph Br 1d	10	34 (84)	60
5	Ph Ph Br 1e	10	30 (72)	58
6 7	Eto Br Br 1f	10 0.6	29 (68) 38 (63)	58 40
8 9	Ph Br 3a	10 50	11 (18) 17 (43)	39 61
10	Ph I <b>3b</b>	10	31 (55)	44
11	Br Br 5a	10	41 (94)	56
12 13	5b	10 0.6	33 (87) 39 (70)	63 44

The reaction of  $C_{60}$  with 10 equiv of benzyl Brothild afford a  $4^{+}$  dibenzylated  $C_{60}$  in low yield (entry 8). In this reaction, the rate of the disappearance of the characteristic absorption peaks of  $C_{60}$  was slower than those of the  $\beta$ -dicarbonyl compounds. In contrast, both the reaction rate and yield of **4** were increased by increasing the amount of benzyl bromide or by using benzyl iodide instead of benzyl bromide (entries 9 and 10). The reaction of  $C_{60}^{-2}$  with an alkyl dihalide is also well known as one of the cycloaddition reactions.<sup>31-33</sup> The reaction of  $C_{60}^{--}$  with **1f** and **5** formed the corresponding cycloaddition products **2a** and **6**, respectively (entries 6, 11, and 12). When the amount of alkyl halide used was decreased, the yields of **2a** and **6** were increased (entries 7 and 13).

To confirm the reaction mechanism,  $C_{60}$  was reacted with 50 equiv of butyl bromide. As shown in Figure S2, it took a longer time for the characteristic absorption peaks assigned to  $C_{60}$  to decrease after the addition of butyl bromide compared with that after the addition of substrates **1**, **3**, and **5**. After the reaction, insoluble materials were obtained along with  $C_{60}$ . This lower reactivity of butyl bromide as compared with that of substrates **1**, **3**, and **5** excludes an  $S_N 2$  reaction mechanism for the reaction of  $C_{60}$ . It is consistent with the low nucleophilicity of  $C_{60}$  due to its  $60\pi$  electron system.

Fukuzumi et al. reported detail studies on the electron transfer from  $C_{60}^{2-}$ ,  $C_{60}^{--}$ , and four semiquinone radical anions to three allyl halides and manganase(III) dodecaphenylporphyrin, and determined the rate constants of these electron transfer reactions.<sup>34</sup> These rate constants showed linear correlation with oxidation potential of donors. The electron transfer rate constants from  $C_{60}$  to acceptors were lower than that from  $C_{60}^{2-1}$ to acceptors depending on its lower oxidation potential. From the comparison of the reduction potential of acceptors, the electron transfer from  $C_{60}$  to **1a** (-1.13 V vs SCE)<sup>35</sup> is energetically feasible than that to allyl bromide (-1.4 V vs SCE).<sup>36</sup> On the other hand, in the case of acceptors having relatively high reduction potential such as benzyl bromide (-1.85 V vs SCE),<sup>37</sup> there is a possibility to form  $C_{60}$  dianion ( $C_{60}^{2-}$ ) via disproportionation of  $C_{60}$ . Recently, Gao et al. reported that the benzylated  $C_{60}$  anion (Bn $C_{60}$ ) was detected by in situ measurements of absorption spectra in the reaction of  $C_{60}^{2-1}$ with benzyl bromide.<sup>38</sup> The characteristic absorption peaks at 954 nm assigned to  $C_{60}^{2-}$  and at 660 nm assigned to  $BnC_{60}^{-}$  were not observed in the reaction of  $C_{60}$ . with benzyl bromide, although the results do not exclude the possibility of contribution of the disproportionation pathway (Figure S2).

Thus, we assume that the reaction proceeds via electron transfer from  $C_{60}$ <sup>-</sup> to the alkyl halide, and the generated alkyl radical then attacks  $C_{60}$ . Subsequent radical coupling reaction of the alkylated  $C_{60}$  radical accompanied by hydrogen abstraction affords **2**. In this hydrogen abstraction, another radical species is required, and two  $C_{60}$ <sup>--</sup> molecules are consumed in the formation of the mono adducts. For the formation of **4** and **6**, addition of the alkyl radical to the alkylated  $C_{60}$  radical intermediates takes place instead of the hydrogen abstraction. Thus, the high recovery of  $C_{60}$  from the reaction is consistent with the proposed reaction mechanism. Very recently, Wang et al. and Hirsch et al. have reported independently, that the

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reaction of  $C_{60}$  with **1a** and **5a** to give **2a** (51%) and **6** (21%), respectively.  $^{\rm 39,40}$  They proposed that the reaction involved a single-electron transfer process from  $C_{60}$ .<sup>-</sup> to the alkyl halides.

It is interesting that the reaction of  $C_{60}$  with  $\beta$ -dicarbonyl compounds affords methanofullerenes selectively, even though the proposed intermediates are similar to the intermediates in the formation of dihydrofuran-fused  $C_{60}$ .<sup>17-22</sup> In the reaction of C<sub>60</sub> with carbonyl compounds promoted by manganese(III) 10 acetate over 80°C, it was proposed that the radical 11 intermediates, alkylated C<sub>60</sub> radicals, afford corresponding 12 enolate salt and oxidized by the manganese(III) to give 13 C<sub>60</sub>.<sup>18-20</sup> Interestingly, dihydrofuran- or lactone-fused 14 methanofullerenes and dihydrofuran-fused C<sub>60</sub> were formed 15 competitively from aromatic methyl ketones in the presence of 16 manganese(III) acetate or cupper(II) acetate.<sup>20</sup> In the related 17 studies reported by X. Gao et al., it was proposed that 18 dihydrofuran-fused C<sub>60</sub> is produced from alkylated C<sub>60</sub> radical in 19 the presence of excessive hydroxide and iodide.<sup>21</sup> Therefore, 20 the results showed that the reaction products are different **≱**1 à2 depending on the reaction methods and additives even if the ä3 intermediates, alkylated C<sub>60</sub> radicals, are the same. 24 25

In summary, the reaction of  $C_{60}$  with alkyl halides and alkyl dihalides was conducted. Methanofullerenes, 1,4-dialkylated C<sub>60</sub>, and cycloaddition products were selectively formed from active methylene compounds, benzyl halides, and alkyl dibromides, respectively. A plausible reaction mechanism for the formation of the products via electron transfer was proposed.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgements

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New reductive alkylation of  $C_{60}$  with  $\alpha$ -bromo-1,3-dicarbonyl compounds, benzyl halide, and 1,2-bis(dihalomethyl)benzene have been reported.



Letter

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