Synthesis of Functionalized Fullerene by Mono-alkylation of Fullerene Cyclopentadienide

Ryo Hamasaki, Yutaka Matsuo, and Eiichi Nakamura*
Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

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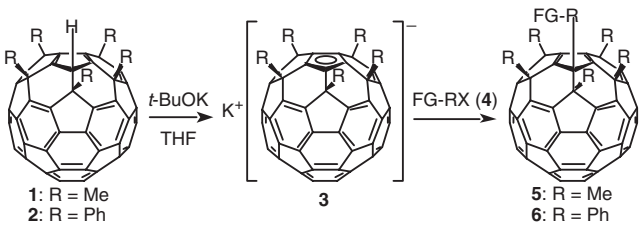
Mono-alkylation reaction of a fullerene cyclopentadienide with a functionalized alkyl halide quantitatively gave a functionalized [60]fullerene derivative that may bear a variety of functional groups and may exhibit high solubility in various solvents.

Functionalization of fullerenes provides the carbon cluster with the properties that are unavailable for the pristine materials.[1] One simple example of such properties is the increased solubility:[2] The creation of water-soluble fullerenes stimulated wide interest among scientists and engineers.[3] Direct introduction of organic groups onto fullerenes, however, is a problem since it almost inevitably gives a mixture of products except two types of reactions, tri- and penta-addition of an organocopper reagent[4] and photo-induced tetra-amination,[5] both of which can be achieved generally in quantitative yield based on the amount of the fullerene molecule used for the reaction. We have for sometime considered that the product of the penta-addition to [60]fullerene (**1** and **2**) serves as a platform for further functionalization.[6–9] Herein we report that mono-alkylation of the these molecules can be achieved quantitatively under mildly basic conditions by the use of a stoichiometric amount of an alkyl halide. The method allows the introduction of a variety of functional groups, which will be useful for applications and can enhance the solubility of the molecules. The overall yield of the two-step synthesis starting from [60]fullerene is generally over 90% yield.



Scheme 1.

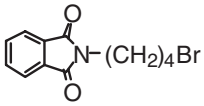
We previously reported that the cyclopentadienyl proton on the penta-adduct **2** is more acidic than water,[10] which suggested to us that the cyclopentadienide **3** is an unreactive nucleophile. Contrary to this naive expectation, we found that this carbanion is very reactive toward organic alkylating reagents. Thus, the penta-methyl anion **3** was found to react with an alkyl iodide within 10 min at room temperature and even with an alkyl chloride within a few hours to give the desired mono-alkylated product in high to quantitative yield (Scheme 1; Table 1, Entries 1–3).

A typical procedure is given for the alkylation of **3** with butyl iodide. A solution of *t*-BuOK in THF (1.0 M, 1.3 mmol, 1.3 mL) was added to a suspension of $C_{60}Me_5H$ (**1**; 95% purity; 1.00 g, 1.26 mmol) in THF (50 mL) at 25 °C. The color of the reaction mixture changed from red to black. Butyl iodide (1.4 mmol) was added to the mixture. After stirring for 1 h, when the reaction was complete, aqueous saturated NH_4Cl (0.5 mL) was added and the solvent was removed under reduced pressure. The residual orange solid was dissolved in 100 mL of toluene and the mixture was filtered through a pad of silica gel. The orange filtrate was concentrated under reduced pressure and was diluted with 500 mL of methanol. The precipitate collected by filtration was 98% pure (1.04 g, 95%) as judged by HPLC analysis. Further purification can be achieved by silica gel column chromatography.

Owing to the low basicity of the anion **3**, the method tolerates a variety of functional groups as shown in Table 1. The presence of alkenyl, alkynyl, free hydroxy, ester, epoxide, and imide groups does not affect at all the efficiency of the reaction. The nucleophilicity of the anion is high enough to allow a secondary alkyl group to be introduced in high yield (Entry 4). Not unexpectedly, however, the reaction with a tertiary halide resulted in the recovery of the starting fullerene (Entry 5).

The reaction of the penta-phenyl compound **2** was expectedly slower than that of **1**, but proceeded in high yield when we

Table 1. Reaction of **1** with various electrophiles

Entry	FG-RX	Product	Yield/%[a]
1	*n*-BuI (**4a**)[b]	**5a**	95
2	*n*-BuBr (**4b**)[b]	**5a**	94
3	*n*-BuCl (**4c**)[c]	**5a**	84
4	*i*-PrI (**4d**)	**5d**	90
5	*t*-BuI (**4e**)[d]	-	-[e]
6	$HC{\equiv}CCH_2Br$ (**4f**)	**5f**	97
7	$H_2C{=}CH(CH_2)_4Br$ (**4g**)	**5g**	100
8	$HO\text{-}(CH_2)_3Br$ (**4h**)	**5h**	93
9	$HC{\equiv}C(CH_2)_4Br$ (**4i**)	**5i**	93
10	$EtOC(=O)(CH_2)_3Br$ (**4j**)	**5j**	92
11	 $(CH_2)_4Br$ (**4k**)	**5k**	96
12	$H_2C{=}CH(CH_2)_6Br$ (**4l**)	**5l**	99
13	 $(CH_2)_6Br$ (**4m**)[c]	**5m**	90

[a]Isolated yield obtained with 1.1 equiv. of the alkyl halide. [b]The reaction was complete within 30 min. [c]The reaction was complete within 2 h. [d]The reaction mixture was refluxed for 2 h. [e]90% recovery of **1**.

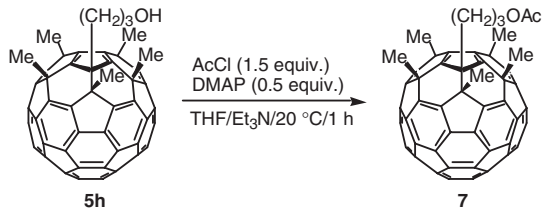
Table 2. Reaction of **2** with various electrophiles

Entry	FG-RX	Product	Yield/%[a]
1	*n*-BuI (**4a**)[b]	**6a**	97
2	AcO-$(CH_2)_4$I (**4n**)	**6n**	95
3	MeOC(=O)$(CH_2)_3$I (**4o**)	**6o**	92
4	H_2C=CH$(CH_2)_6$I (**4p**)	**6p**	90

[a]Isolated yield obtained with 1.1 equiv. of alkyl halide in refluxing THF for 4 h. [b]The reaction time is 2 h.

used an alkyl iodide in refluxing THF. Under these conditions, we could also introduce various functional groups by using 1.1 equiv. of the necessary alkylating reagent (Table 2).

The products listed in Table 1 are expected to be useful for further functionalization.[11] For instance, quantitative conversion of the alcohol **5h** to the corresponding acetate can be readily achieved. The overall yield of the ester from [60]fullerene is 85% (Scheme 2).



Scheme 2.

Finally we examined the effect of the functionalization on the solubility. We took the compounds **5h** and **5j** and compared their solubility with [60]fullerene[2] and the compound **1**. As summarized in Table 3, the functionalized compounds show markedly increased solubility in a variety of polar solvents. The 100 mg/mL solubility of the penta-methyl mono-ethoxycarbonylpropyl compound **5j** is noteworthy, making this type of compounds promising candidates as additives in plastics and photoresist materials.[12]

In conclusion, we have developed a procedure that allows the coupling of a (potentially) precious functionalized alkyl group to a fullerene skeleton under 1:1 stoichiometry and under mildly basic conditions (note that the cyclopentadienide **3** is less basic than water).[6] We expect that one can make the whole process even more practically useful by combining the penta-addition of an organocopper reagent and the present alkylation in a single pot since the first addition generates in situ a copper cyclopentadienide corresponding to **3**. Such an engineering improvement will be examined in the later stage of the development of our studies.

Table 3. The solubilities of C_{60}, **1**, **5h** and **5j** to common organic solvents[a]

	C_{60}	**1**	**5h**	**5j**
THF	0.0[b]	9.1	59.7	103.0
$CHCl_3$	0.2[b]	5.2	21.0	35.9
DMF	0.0	0.5	44.4	15.4
EtOAc	0.0	0.0	6.0	3.9

[a]Solubility in mg/mL. [b]Ref. 2.

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