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Efficient conversion of bromofullerene to alkoxyfullerenes through either homolytic or heterolytic cleavage of C_{60}–Br bond

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Abstract—The bromine atom in a fullerene-mixed peroxide derivative is replaced by an alkoxyl group under visible light irradiation or in the presence of silver salt. Homolytic or heterolytic cleavage of the C_{60}–Br bond is proposed to explain the mechanism. The presence of oxygen is also a key factor in the photolysis reaction.
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1. Introduction

Halogenation is one of the well studied fullerene reactions.[1] Numerous halofullerenes have been reported through various halogenation methods, some of which exhibit unique structure such as $C_{50}Cl_{10}$.[2] In light of the rich chemistry of classical organic halides, halofullerenes have much potential for further functionalization. Taylor et al. found that the hexachlorofullerene $C_{60}Cl_6$ can be converted to $C_{60}(Cl)(Ph)_5$ in benzene in the presence of ferric chloride.[3] Heating $C_{60}Cl_6$ with either methanol or propan-2-ol yields *para*-$(MeO)_2C_{60}$ and *para*-$(^iPrO)_2C_{60}$, respectively. When $C_{60}Cl_6$ was treated with ROH–NaOR, alkoxyfullerenes $C_{60}(Cl)(OR)_5$ (R=Me, Et) were obtained in moderate yields.[4] But wide application of halofullerenes as precursors for other fullerene derivatives is difficult due to poor selectivity and low yields.[5] Conclusive structure assignment of partially replaced halofullerene is also a challenging problem, which usually requires single crystal X-ray analysis data. Mechanisms of halogen replacement reactions are not clear in most cases. Isomerically pure alkoxyfullerenes are still limited compared to other fullerene derivatives.[6]

We have synthesized a number of fullerene-mixed peroxides, some of which contain one or two halogen atoms in addition to the *tert*-butylperoxo groups.[7] The presence of the *tert*-butyl groups in these compounds greatly facilitates purification and characterization as a result of much improved solubility, thus providing the opportunity to explore the reaction mechanism. Here we report the selective replacement of the bromine atom in compound **1** by alkoxyl groups under photolysis or in the presence of silver salts.

Visible light irradiation of **1** in a mixture of CH_2Cl_2 and ROH gave the corresponding bromo replaced products **2a**–**c** in good yields (Scheme 1). A large excess of the alcohol was necessary to shorten the reaction time and improve the yields (1 ml alcohol for 35 mg of compound **1**). The reactions were usually finished within 20 min. Prolonged irradiation resulted in partial decomposition of compounds **2**. Oxygen is also a key factor. If nitrogen was bubbled through the solution for 10 min before the irradiation, the reaction was slower and other by-products could be detected by TLC (the isolated yield of **2a** was 56%). On the other hand, bubbling oxygen through the solution led to over reaction and mixture of products. Atmosphere oxygen appeared to be the optimal condition. In the case of **2d**, photolysis gave poor results perhaps due to decomposition of ^{t}BuOOH under irradiation. The relatively low yield of the benzyl alcohol reaction under photolysis is probably due to singlet oxygen oxidation of the methylene group leading to other by-products. After the photolysis, the high boiling benzyl alcohol was separated by extraction from $CS_2/MeOH/H_2O$. This procedure also caused some loss of product **2c**.

The same product could also be obtained by silver mediated cleavage of C_{60}–Br bond. In this case, a 12-fold alcohol was enough to obtain moderate to good yields (Scheme 1). Large excess of alcohol resulted in longer reaction time and slightly improved yields. The excess alcohol probably coordinates to

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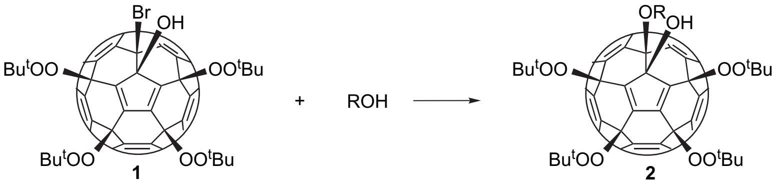


	R	Condit.	ROH^a	Time	Yield (%)
2a	Me	hν	1 (ml)	10 min	95 (72)^b
		Ag_2CO_3	0.4 (mmol)	45 min	87 (79)
			1 (ml)	3 h	98 (78)
2b	Et	hν	1 (ml)	15 min	91 (60)
		Ag_2CO_3	0.4 (mmol)	1.5 h	89 (72)
			1 (ml)	8 h	94 (76)
2c	Bn	hν	1 (ml)	20 min	41 (30)
		Ag_2CO_3	0.4 (mmol)	3.5 h	91 (72)
2d	^{t}BuO	Ag_2CO_3	5.5 mmol	2 h	89 (86)

[a] for 35 mg (0.03 mmol) of compound **1**. [b] The higher yield was calculated according to converted starting material **1**, isolated yield in the bracket was calculated according to the total amount of starting material **1**.

Scheme 1. Alkoxylation of bromofullerene.

the silver ion thus slowing down its interaction with the bromine atom. Silver carbonate gave the best result compared with other silver salts. Silver acetate cleaved the C_{60}–Br bond effectively, but the nucleophilic acetate anion competes with the alcohol to give fullerene acetate derivatives. Similarly the nitrate anion of silver nitrate competes with the alcohol and gave the nitrate derivative **2e**. In the absence of alcohol, the nitrate derivative was obtained in almost quantitative yield (Scheme 2). Trace amount of the epoxide derivative $C_{60}(O)(OO^tBu)_4$ **3** could be detected in both the photolysis and silver mediated reactions.

Compound **2e** was prepared previously by treating the epoxide derivative **3** with nitric acid.[8] Locations of the hydroxyl and nitrosylate groups were deduced from their spectroscopic data. We have now obtained its single crystal X-ray diffraction structure (Fig. 1), which confirmed our previous assignment. The hydroxyl group is on the central pentagon and forms H-bond with the adjacent peroxo oxygen atom. The bonding distances are 1.01 (O1–H) and 1.99 (O3–H) Å, and the angle for ∠OHO is 151°.

Two pathways are suggested for the above reactions as shown in Scheme 3. In the photolysis reaction, the first step is homolysis of the C_{60}–Br bond to form the radical intermediate B, which is then oxidized to the cation A. The oxidant could be singlet oxygen since fullerene and its derivatives are known to be good sensitizers for singlet oxygen.

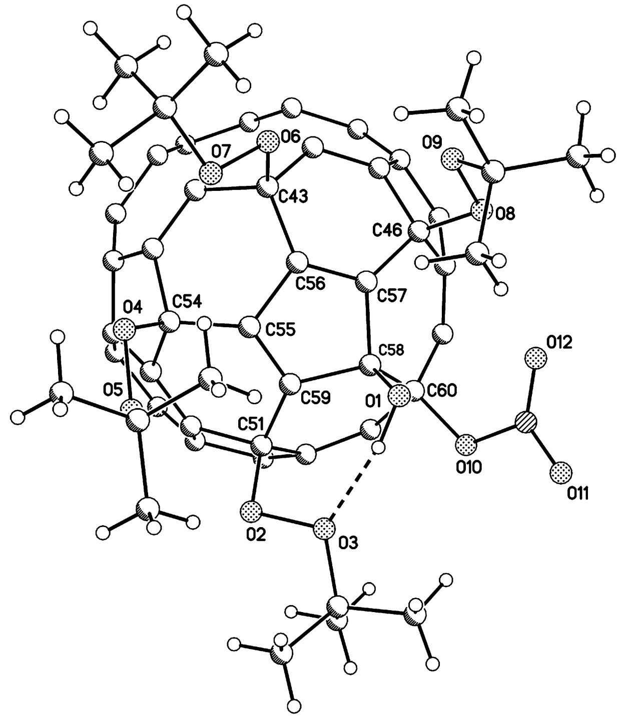
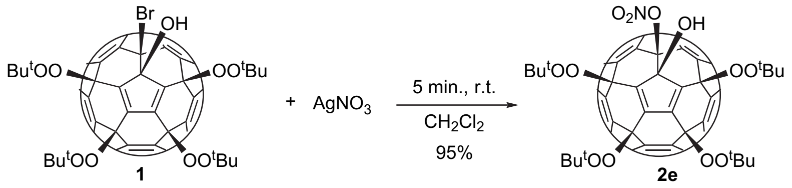
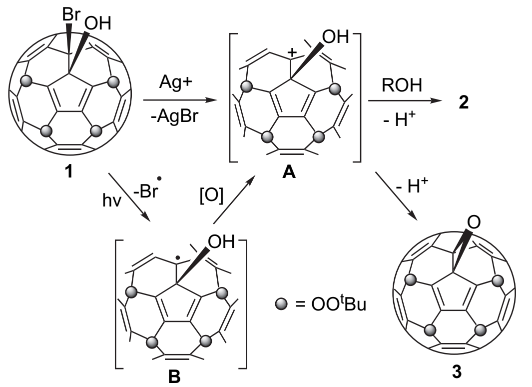


Figure 1. Single crystal X-ray structure of **2e** (for clarity some carbon atoms on the C_{60} cage were omitted).



Scheme 2. Formation of fullerene nitrate derivative.



Scheme 3. Proposed pathway for the bromine replacement reactions.

Oxygen has been shown to oxidize azafullerene radical $C_{59}N^{\bullet}$ to the cation $C_{59}N^{+}$ readily under visible light irradiation.[9] Addition of alcohol to the cation A and subsequent deprotonation gives the final alkoxyl derivative **2**. In the silver mediated reaction, the cation intermediate A is formed directly through heterolysis of the C_{60}–Br bond. Similar one-step formation of intermediate A under photolysis is unlikely since presence of oxygen was needed to convert **1** to **2** as mentioned above. Formation of trace amount of epoxide **3** is apparently due to intramolecular addition of the adjacent hydroxyl group to the carbocation.

The above pathway is reminiscent to results reported in the literature. Stable fullerene cations, similar to the present intermediate A, have been observed before.[10] Monoalkylated fullerene cations $R–C_{60}^{+}$ have stability comparable to that of *tert*-butyl cation.[11] Quenching the cation $R–C_{60}^{+}$ with methanol yielded single isomer $C_{60}(OMe)R$ ($R{=}CHCl_2$ or CCl_2CH_2Cl).[10a] Lewis acids such as ferric chloride or aluminum chloride were used to initiate halogen fullerene bond heterolytic cleavage besides $AgBF_4$. For the present fullerene-mixed peroxides, ferric chloride and aluminum chloride attack the peroxide preferentially to cleave the O–O bond and form homofullerene derivatives.[7b]

In conclusion, halofullerene to alkoxylfullerene conversion has been achieved in good yields through homolytic or heterolytic cleavage of the C_{60}–Br bond. The method provides a new route to synthesize isomerically pure alkoxyfullerene derivatives. Further work is underway to explore the present method using other halofullerene derivatives.

2. Experimental section

2.1. General

All reagents were used as received. CH_2Cl_2 used for reactions was distilled from P_2O_5. Other solvents were used as received. The reactions were carried out under atmosphere. Compound **1** was prepared as in the literature.[7c] Preparation of compounds **2a**, **2b**, **2d**, and **2e** was carried out analogously. The preparation of **2a** is shown below as an example. Compounds **2a**, **2b**, **2d**, **2e**, and **3** were characterized by comparing their NMR data with those we have reported previously.[7b,8]

2.2. Photolysis reaction

The bromofullerene derivative **1** (34.7 mg, 0.0296 mmol) was dissolved in dry dichloromethane (4 mL). Anhydrous methanol (1 mL) was added. The mixture was stirred and irradiated with a luminescent light bulb (12 W) at room temperature. Progress of the reaction was monitored by TLC. After about 10 min, the mixture was evaporated and then separated by column chromatography on silica gel. Elution with toluene and petroleum (2:1) gave trace of the epoxide derivative $C_{60}(O)(OO^{t}Bu)_4$ **3** as the first band, unreacted compound **1** (8.5 mg, 0.0725 mmol) as the second band, and the product **2a** (23.9 mg, 0.0227 mmol) as the third band. Yield: 72%, yield based on consumed starting material: 95%.

2.3. Silver mediated reaction

Compound **1** (35 mg, 0.0299 mmol) was dissolved in dry dichloromethane (5 mL), methanol (12 mg, 0.375 mmol) and Ag_2CO_3 (200 mg, 0.725 mmol) were added. The mixture was stirred at room temperature in dark. Progress of the reaction was monitored by TLC. After about 45 min, the mixture was transferred directly into a short column of silica gel and eluted with dichloromethane to get rid of Ag_2CO_3. The eluted solution was evaporated and then separated by column chromatography on silica gel. Elution with toluene and petroleum (2:1) gave trace of the epoxide derivative $C_{60}(O)(OO^{t}Bu)_4$ **3** as the first band, unreacted compound **1** (3 mg, 0.003 mmol) as the second band, and product **2a** (26.6 mg, 0.0237 mmol) as the third band. Yield: 79%, yield based on consumed starting material: 87%.

Purification procedure of **2c** was slightly different from above due to the higher boiling point of benzyl alcohol. After the reaction finished, the mixture was evaporated. The residue contained unreacted benzyl alcohol, which could not be separated from the products by column chromatography directly. Benzyl alcohol was separated from the fullerene products by adding methanol, water, and CS_2 sequentially to the residue. The CS_2 phase contained the fullerene derivatives while the methanol/water phase contained most of the benzyl alcohol. The CS_2 solution was evaporated and the residue was then separated by column chromatography on silica gel. Characterization data for compound **2c** are the following.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51–7.50 (m, 2H), 7.35–7.33 (m, 3H), 5.26 (s, 2H), 4.70 (s, 1H), 1.48 (s, 18H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.67, 150.02, 149.13, 149.01, 148.67, 148.60, 148.44, 148.40, 148.36, 147.67, 147.51, 147.46, 147.35, 146.98, 145.86, 145.38, 144.97, 144.95, 144.40, 144.37, 144.01, 143.88, 143.36, 142.97, 142.74, 141.31, 138.59, 137.86, 128.62, 128.30, 127.90, 82.54, 82.41, 82.21, 81.85, 81.34, 80.94, 72.54, 26.76, 26.68. FTIR (microscope): 3518, 2979, 2930, 1455, 1387, 1192, 1093, 1051, 1020, 871, 732 cm^{-1}. ESIMS: *m/z* (intensity, %): 1218 (20) $[M+NH_4^{+}]$, 803 (100) $[C_{60}(O)_3(OH)_2+H^{+}]$.

2.4. Crystal data for 2e

$C_{76}H_{37}NO_{12}$, $M{=}1156.07$, monoclinic, $P2(1)/c$, $a{=}18.928(4)$, $b{=}14.323(3)$, $c{=}19.360(4)$ Å, $\alpha{=}90$, $\beta{=}102.79(3)$, $\gamma{=}90°$,

V=5118.2(18) Å^3, T=143(2) K, Z=4, ρ_{calcd}=1.50 Mg/m^3, graphite monochromatized Mo Kα-radiation, λ=0.71073 Å, crystal size 0.45×0.20×0.15 mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 8944 unique reflections (R_{int}=0.0577). Refinement on F^2, final residuals R_1=0.0495 for 4589 reflections with I>2σI), wR_2=0.1106 for all data. CCDC-633219 contains the supplementary crystallographic data for this paper.

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Supplementary data

NMR, MS, and IR spectra for **2c** and crystallographic data in CIF format for **2e**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.070.

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