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The Oxidation of Fullerene[C_{60}] using Several Oxidants under Microwave Irradiation

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마이크로파 조건에서 여러가지 산화제를 이용한 풀러렌[C_{60}]의 산화반응

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ABSTRACT : Synthesis of fullerene oxides[$C_{60}(O)_n$] (n=1~4 or n=1) by fullerene[C_{60}] and several oxidants such as 3-chloroperoxy benzoic acid, benzoyl peroxide, trichloroisocyanuric acid, and chromium(VI) oxide took place under microwave irradiation. The reactivity in solid state of fullerene[C_{60}] with various oxidants under same microwave condition increased in order of 3-chloroperoxy benzoic acid > benzoyl peroxide > trichloroisocyanuric acid≒chromium(VI) oxide. The MALDI-TOF-MS, UV-visible spectra and HPLC analysis confirmed that the products of fullerene oxidation were [$C_{60}(O)_n$] (n=1~4 or n=1).

요 약 : 풀러렌[C_{60}]은 3-chloroperoxy benzoic acid, benzoyl peroxide, trichloroisocyanuric acid, chromium(VI) oxide 등의 산화제를 사용하여 마이크로파 조건에서 반응시켜 풀러렌 산화물 [$C_{60}(O)n$](n=1~4 or n=1)을 합성 하였다. 동일한 마이크로파 조건에서 여러 가지 산화제와 풀러렌[C_{60}]의 고체상태 반응성은 3-chloroperoxy benzoic acid > benzoyl peroxide > trichloroisocyanuric acid≒chromium(VI) oxide 순으로 증가함을 나타냈다. MALDI-TOF-MS, UV-visible, 그리고 HPLC를 사용하여 분석한 결과 생성된 풀러렌 산화물은[$C_{60}(O)_n$] (n=1~4 or n=1)임을 알 수 있었다.

Keywords : Fullerene Oxides[$C_{60}(O)_n$] (n=1~4 or n=1), Several Oxidants, Microwave Irradiation, MALDI-TOF-MS

Ⅰ. Introduction

Microwave synthesis is a new technique for conducting chemical reactions space.[1] Microwave irradiated reactions have been given a lot of attention and proven to be a useful synthetic technique for a variety of chemical reactions.[2] The reactions under microwave irradiation sometimes proceed faster than conventional heating reactions[3] and, in many cases, microwave techniques have been shown to be more effective than conventionally conducted reactions. Moreover, in a number of applications, reactions under microwave conditions can provide pure products in high yield.[1]

Also, one of the merit points of a microwave irradiated reaction is the solvent free condition.[4]

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Microwave-assisted solvent free reactions have been widely investigated in chemical synthesis.[5] Many reactions have been accelerated by the use of microwaves.[6] Thus the microwave assisted process will be of interest to many chemist who work with fullerene chemistry. The very rapid rise of temperature of the reactants by microwave irradiation favors some reaction pathways over others and thus leads to selectivity and hence cleaner products.[7] This methodology is expected to be applicable to the simple and efficient preparation of fullerene oxides under microwave irradiation. The reactivity of the fullerenes,[8] C_{60} in particular, with both microwave irradiation and an oxidizing agent is likely to be an important consideration in any technological application of these substances. The $[C_{60}(O)_n]$ (n=1~4) has been obtained by a number of oxidation processes in solid state species. These include the photo-oxygenation of C_{60},[9,10] the electrochemical oxidation of C_{60},[11] the addition of dimethyldioxirane to C_{60},[12] the ozonolysis of C_{60},[13] and the ultrasound induced oxidation of C_{60}.[14] In this paper, we reported a novel, simple and efficient method for the preparation of fullerene oxides with the formation of $[C_{60}(O)_n]$ (n=1~4 or n=1) by the reaction of the fullerene $[C_{60}]$ with several kind of oxidants such as 3-chloroperoxy benzoic acid, benzoyl peroxide, trichloroisocyanuric acid, and chromium(VI) oxide, in solid state under microwave irradiation.

Ⅱ. Experimental

Fullerene $[C_{60}]$ used in this work was 99.0% purity of Tokyo Chemical Inc (TCI). The Oxidants used were 3-chloroperoxy benzoic acid (Fluka, 99.0%), benzoyl peroxide (Fluka, 99.0%), trichloroisocyanuric acid (Aldrich, 99.0%), and chromium (VI) oxide(Aldrich, 97.0%). The microwave irradiation was conducted in multimode with continuous heating at full power by a domestic oven (2450 MHz,700W). Samples were analyzed by MALDI-TOF -MS (Voyager-DE STR) and the matrix was a cyano-4-hydroxy cinnamic acid. HPLC analysis was performed with a Shisedo nanospace SI-2 model. Column was used a cosmosil 5μPBB (250 X 4.6 mm) made by Phenomenex. UV-detector was used at 330 nm. The flow rate was 1.0 ml/min during the mobile phase for toluene/hexane was at the ratio of 6:4(v/v). The injection volume was 10.00 $\mu\ell$ at pump pressure of 3.0 Mpa. The electronic absorption spectra was obtained by UV-visible spectrophotometer (Shimadzu UV-1601 PC).

1. The reaction of fullerene $[C_{60}]$ with 3-chloroperoxy benzoic acid by microwave irradiation.

The mixture of fullerene $[C_{60}]$ (20 mg, 0.028 mol) and 3-chloroperoxy benzoic acid(48.0 mg, 0.28 mol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture of the fullerene $[C_{60}]$ and 3-chloroperoxy benzoic acid was poured into a 50 ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

2. The reaction of fullerene $[C_{60}]$ with benzoyl peroxide by microwave irradiation.

The mixture of fullerene $[C_{60}]$ (20 mg, 0.028 mol) and benzoyl peroxide (68.0 mg, 0.28 mol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture of the fullerene $[C_{60}]$ and benzoyl peroxide was poured into a 50 ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

3. The reaction of fullerene$[C_{60}]$ with trichloroisocyanuric acid by microwave irradiation.

The mixture of fullerene $[C_{60}]$ (20 mg, 0.028 mol) and trichloroisocyanuric acid (65.0 mg, 0.28 mol)

was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture of the fullerene[C_{60}] and trichloroisocyanuric acid was poured into a 50 ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

4. The reaction of fullerene [C_{60}] with chromium(VI) oxide by microwave irradiation.

The mixture of fullerene [C_{60}](20 mg, 0.028 mol) and chromium(VI) oxide (28.0 mg, 0.28 mol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture of the fullerene [C_{60}] and chromium(VI) oxide was poured into a 50 ml round bottom flask. The flask was placed into the microwave oven and irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

Ⅲ. Results and discussion

The microwave irradiated process applied to the synthesis of fullerene oxides by the reaction of fullerene[C_{60}] with several oxidants such as 3-chloroperoxy benzoic acid, benzoyl peroxide, trichloroisocyanuric acid, and chromium(VI) oxide, which gives rise to the oxidation of fullerene [C_{60}] at 120~140℃ under microwave irradiated conditions with the formation of [$C_{60}(O)_n$] (n=1~4 or n=1).

For many chemical syntheses, the development of microwave assisted solvent-free procedures has led to enhanced reaction rates compared to conventional heating. The MALDI-TOF-MS spectra and HPLC profile revealed that the oxidation of fullerene [C_{60}] took place when it was subjected to microwave irradiation in the presence of oxidants. The reactivity of fullerene [C_{60}] under microwave irradiated conditions increased in the order of 3-chloroperoxy benzoic acid > benzoyl peroxide > trichloroisocyanuric acid ≅ chromium(VI) oxide. The difference between various oxidation reactions with and without microwave irradiation is as follows; the reaction time is shortened due to high pressure and temperature under microwave condition. Epoxidation mediated by microwave irradiation with various oxidants is efficient for both electron-rich olefins and fullerenes. The MALDI-TOF-MS and HPLC analysis data reported in Table 1 show the formation of [$C_{60}(O)_n$](n=1~4 or n=1). The MALDI-TOF MS analysis reported in Figure 1 shows the formation of [$C_{60}(O)_n$](n=1~4 or n=1) observed at m/z 720 (C_{60}), 736($C_{60}O_1$), 752($C_{60}O_2$), 768($C_{60}O_3$), 784 ($C_{60}O_4$) in the MALDI-TOF MS spectrum. The most intense peak was at m/z 720 in the MALDI-TOF-MS spectrum in Figure 1 (a)~(d) which is due to the unreacted fullerene [C_{60}] and the fragmentation of fullerene oxide [$C_{60}(O)_n$](n=1~4 or n=1). The HPLC chromatogram (figure 2) is for the most oxidated fullerene oxides by fullerene[C_{60}] with 3-chloroperoxy benzoic acid, which showed C_{60}, $C_{60}O_1$, $C_{60}O_2$, $C_{60}O_3$, $C_{60}O_4$ at different retention times, respectively.

Comparing oxidation of fullerenes [$C_{60,}$ C_{70}] between C_{60} and C_{70}, the reactivity of C_{70}[15] by microwave irradiation with various oxidants such as 3-chloroperoxy benzoic acid, benzoyl peroxide, trichloroisocyanuric acid, and chromium(VI) oxide looks lower than that of C_{60} under similar reaction condition. The reactivity difference probably results from the increase of hexagons in their structure.[16]

The electronic absorption bands (λ_{max}) of [$C_{60}(O)_n$] (n= 1~4) and pure C_{60} in benzene were observed at 278, 334, and 407 nm in the mixture of[$C_{60}O_n$] (n=1~4) and at 278, 336, and 407 nm in pure C_{60} (in figure 3). Due to the breaking of the conjugated 6-6 ring junction by addition of oxygen in the fullerene[C_{60}], the bands of electronic absorption moved into blue shift. By the additional breaking of the carbon-carbon double bond in the fullerene[C_{60}], the wave length of absorption bands changed and became lower (336 nm→334 nm) in

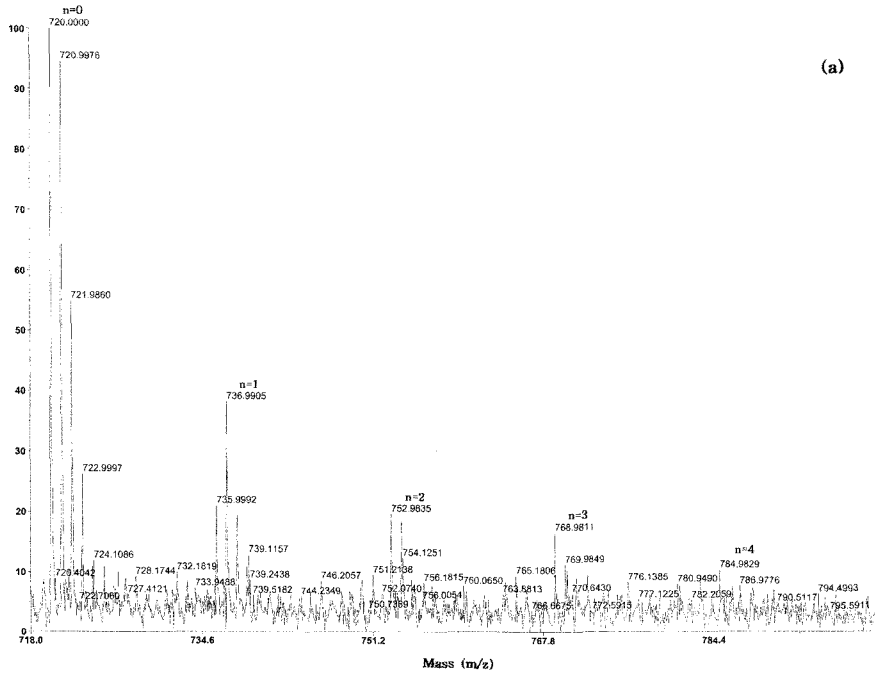
Table 1. The MALDI-TOF-MS and HPLC Analysis of $C_{60}(O)_n$ (n=1~4 or n=1) Produced by Microwave Irradiation for 20 min.

Oxidants	Fullerene	Formation of $C_{60}(O)_n$ (n=1~4 or n=1)	Mass unit (m/z)	Retention times, min
3-chloroperoxy benzoic acid	C_{60}	$C_{60}O_4$	784	10.77
		$C_{60}O_3$	768	11.32
		$C_{60}O_2$	752	11.81
		$C_{60}O_1$	736	12.25
		C_{60}	720	12.61
Benzoyl peroxide	C_{60}	$C_{60}O_3$	768	11.31
		$C_{60}O_2$	752	11.80
		$C_{60}O_1$	736	12.21
		C_{60}	720	12.62
Trichloro - isocyanuric acid	C_{60}	$C_{60}O_2$	752	11.80
		$C_{60}O_1$	736	12.05
		C_{60}	720	12.61
Chromium(VI) oxide	C_{60}	$C_{60}O_2$	752	11.68
		$C_{60}O_1$	736	12.07
		C_{60}	720	12.61

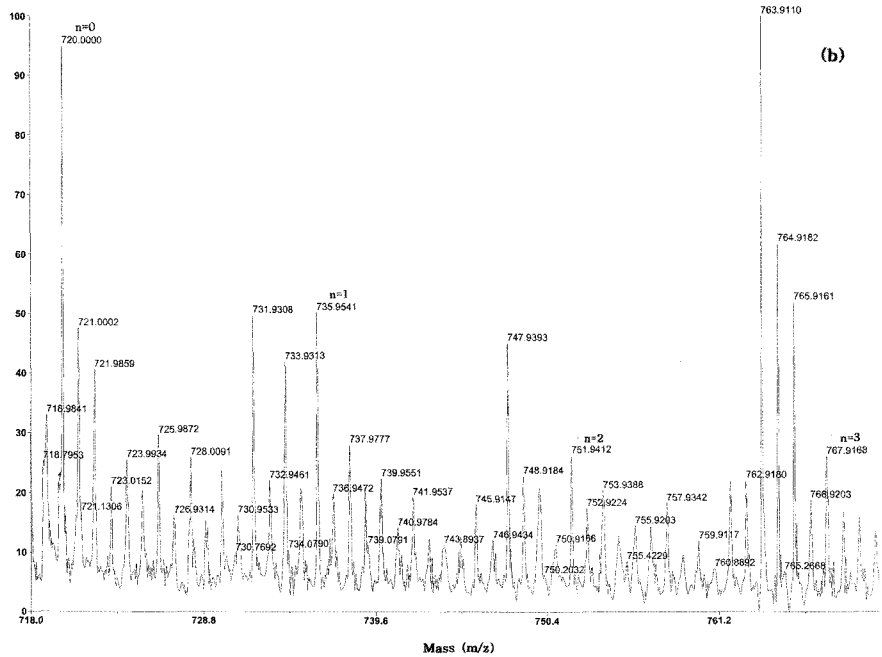
the UV-visible spectrum. This electronic absorption spectrum of the oxidation of fullerene[C_{60}] by microwave irradiation with various oxidants is not same to that of pure C_{60} as the number of oxygen atom increases. This indicates that the multiepoxide of fullerene [C_{60}] perturbs the molecular orbital in pure C_{60}, while the monoepoxide of fullerene [C_{60}] dose not seriously perturb the molecular orbital in pure C_{60}. Also, the peak height of 334 nm in [$C_{60}(O)_n$] (n=1~4) is lower than the peak height of pure C_{60} which was 336 nm as we compared to peak heights. The reaction of fullerene[C_{60}] by microwave irradiation with various oxidants may proceed by the nucleophilic attack of various oxidants at the 6-6 bond(6-6 ring junction) in the fullerene[C_{60}], followed by the heterolytic cleavage of the O-O bond. The consensus mechanism for fullerene oxidation by microwave irradiation with various oxidants, involves oxygen atom transfer to the fullerene[C_{60}]. It is suggested that the fullerene epoxide [$C_{60}(O)_n$](n=1~4 or n=1) may be used as oxygen transfer material. Also, the fullerene oxide, [$C_{60}(O)_n$](n=1~4 or n=1) is an interesting starting material for the formation of other fullerene-based entities.

Ⅳ. Conclusions

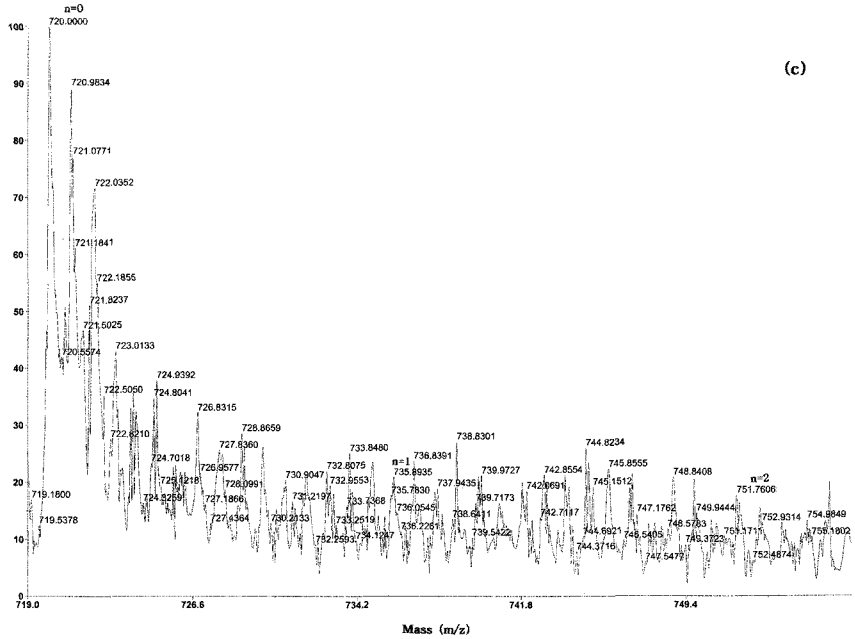
By the HPLC profile, UV-visible and MALDI-TOF-MS spectra of products which were obtained by microwave irradiated oxidation we have identified the [$C_{60}(O)_n$](n=1~4 or n=1) formed in the reaction of C_{60} by microwave irradiation with 3-chloroperoxy benzoic acid, benzoyl peroxide, trichloroisocyanuric acid, and chromium(VI) oxide at 120~140℃. These reaction are of the microwave induced chemical oxidation type in solid state. The reactivity in solid state of fullerene[C_{60}] with various oxidants under same microwave condition showed increasing in order of 3-chloroperoxy benzoic acid > benzoyl peroxide > trichloroisocyanuric acid ≅ chromium(VI) oxide. The epoxidation of olefin by the multiepoxides of fullerene, [$C_{60}(O)_n$](n=1~4 or n=1) is presently under investigation.



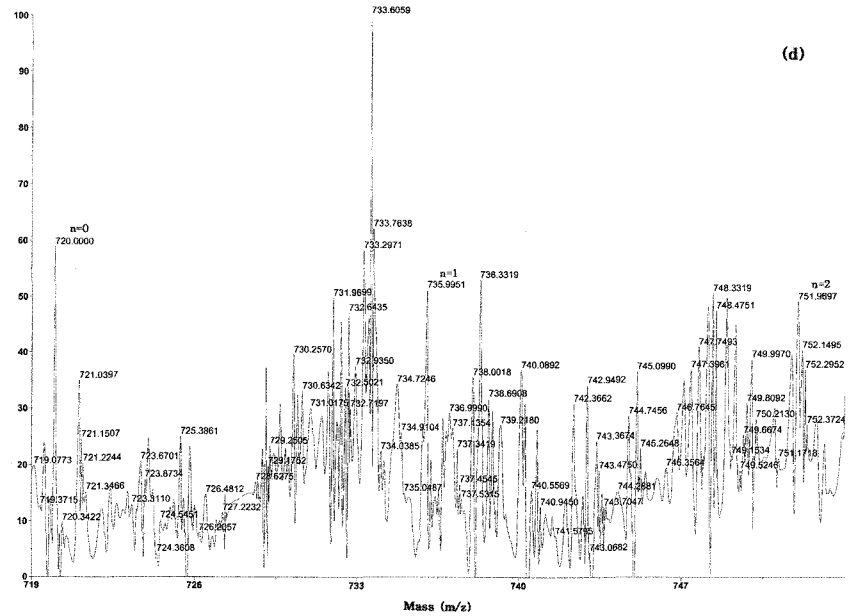
(a) The reaction products of fullerene[C_{60}] with 3-chloroperoxy benzoic acid, n=0, 1, 2, 3, 4 by microwave irradiation shows the presence of C_{60}, $C_{60}O_1$, $C_{60}O_2$, $C_{60}O_3$, $C_{60}O_4$.



(b) The reaction products of fullerene[C_{60}] with chromium(VI) oxide, n=0, 1, 2, 3 by microwave irradiation shows the presence of C_{60}, $C_{60}O_1$, $C_{60}O_2$, $C_{60}O_3$.



(c) The reaction products of fullerene[C_{60}] with trichloroisocyanuric acid, n=0, 1, 2 by microwave irradiation shows the presence of C_{60}, $C_{60}O_1$, $C_{60}O_2$.



(d) The reaction products of fullerene[C_{60}] with benzoyl peroxide, n=0, 1, 2 by microwave irradiation shows the presence of C_{60}, $C_{60}O_1$,$C_{60}O_2$.

Figure 1. MALDI-TOF MS spectra of [$C_{60}(O)_n$] (n=1~4 or n=1).

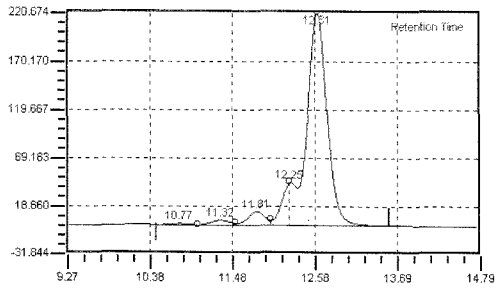


Figure 2. HPLC chromatogram of fullerene oxides; [$C_{60}(O)_n$] (n=1~4).

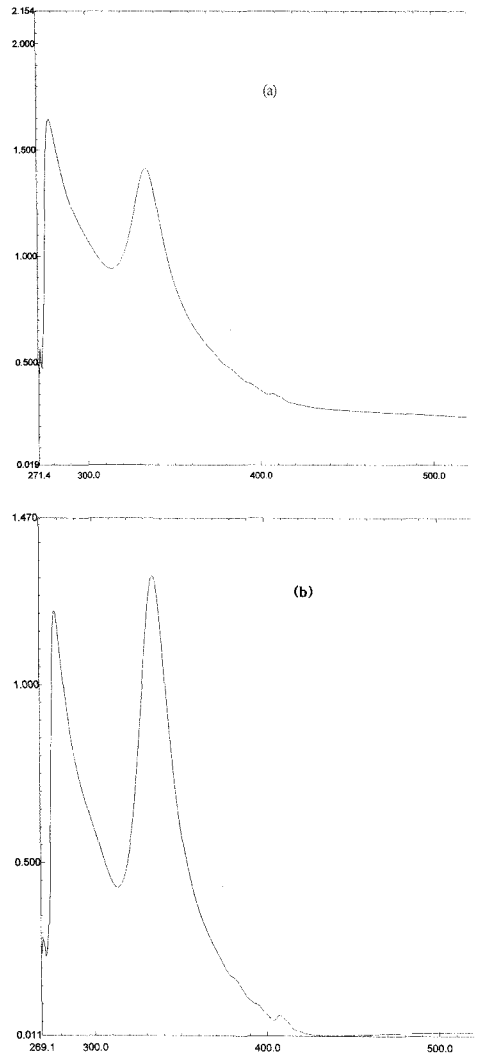


Figure 3. UV-visible spectrum of fullerene oxides; (a)[$C_{60}(O)_n$] (n=1~4), (b)pure C_{60}.

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